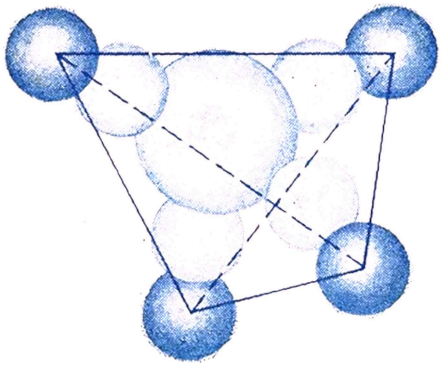
N. AKHMETOV

General and Inorganic Chemistry



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MENDELEEV'S PERIOD
(the longer

Period	Group IA	IIA	IIIB*	Families													
				58	59	60	61	62	63	64	65	66	67	68	69
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
				$4f^{1}6s^{2}$	$4f^{3}6s^{2}$	$4f^{4}6s^{2}$	$4f^{5}6s^{2}$	$4f^{6}6s^{2}$	$4f^{7}6s^{2}$	$4f^{7}5d^{1}6s^{2}$	$4f^{9}6s^{2}$	$4f^{10}6s^{2}$	$4f^{11}6s^{2}$	$4f^{12}6s^{2}$	$4f^{13}6s^{2}$
				140,12	140,907	144,24	[145]	150,4	151,96	157,25	158,925	162,50	164,930	167,26	168,934
				90	91	92	93	94	95	96	97	98	99	100	101
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md
				$6d^{2}7s^{2}$	$5f^{2}6d^{1}7s^{2}$	$5f^{3}6d^{1}7s^{2}$	$5f^{4}6d^{1}7s^{2}$	$5f^{6}7s^{2}$	$5f^{7}7s^{2}$	$5f^{7}6d^{1}7s^{2}$	$5f^{9}7s^{2}$	$5f^{10}7s^{2}$	$5f^{11}7s^{2}$	$5f^{12}7s^{2}$	$5f^{13}7s^{2}$
				232,038	231	238,03	[237]	[242]	[243]	[247]	[247]	[251]	[254]	[253]	[258]

The Periodic law '... expresses the properties of elements rather than of simple bodies. The properties of simple and complex bodies depend in a periodic manner on the atomic weight of the elements solely because ... these properties are themselves the result of the properties ... of the elements forming the bodies'.

D. I. Mendeleev

TABLE OF THE ELEMENTS
ion of the table)

of elements

	IVB	VB	VIB	VIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
												1 H $1s^1$ 1,0079	2 He $1s^2$ 4,0026
								5 B $2s^22p^1$ 10,81	6 C $2s^22p^2$ 12,011	7 N $2s^22p^3$ 14,0067	8 O $2s^22p^4$ 15,9994	9 F $2s^22p^5$ 18,9984	10 Ne $2s^22p^6$ 20,179
								13 Al $3s^23p^1$ 26,98154	14 Si $3s^23p^2$ 28,086	15 P $3s^23p^3$ 30,9737	16 S $3s^23p^4$ 32,06	17 Cl $3s^23p^5$ 35,453	18 Ar $3s^23p^6$ 39,948
	22 Ti $3d^24s^2$ 47,90	23 V $3d^34s^2$ 50,941	24 Cr $3d^54s^1$ 51,996	25 Mn $3d^54s^2$ 54,9380	26 Fe $3d^64s^2$ 55,847	27 Co $3d^74s^2$ 58,9332	28 Ni $3d^84s^2$ 58,70	29 Cu $3d^{10}4s^1$ 63,54	30 Zn $3d^{10}4s^2$ 65,38	31 Ga $4s^24p^1$ 69,72	32 Ge $4s^24p^2$ 72,59	33 As $4s^24p^3$ 74,9216	34 Se $4s^24p^4$ 78,96	35 Br $4s^24p^5$ 79,904	36 Kr $4s^24p^6$ 83,80
	40 Zr $4d^25s^2$ 91,22	41 Nb $4d^45s^1$ 92,906	42 Mo $4d^55s^1$ 95,94	43 Tc $4d^55s^2$ [97]	44 Ru $4d^75s^1$ 101,07	45 Rh $4d^85s^1$ 102,905	46 Pd $4d^{10}$ 106,42	47 Ag $4d^{10}5s^1$ 107,868	48 Cd $4d^{10}5s^2$ 112,40	49 In $5s^25p^1$ 114,82	50 Sn $5s^25p^2$ 118,69	51 Sb $5s^25p^3$ 121,75	52 Te $5s^25p^4$ 127,60	53 I $5s^25p^5$ 126,9045	54 Xe $5s^25p^6$ 131,30
71 Lu $4f^{14}5d^16s^2$ 174,97	72 Hf $5d^26s^2$ 178,49	73 Ta $5d^36s^2$ 180,948	74 W $5d^46s^2$ 183,85	75 Re $5d^56s^2$ 186,207	76 Os $5d^66s^2$ 190,2	77 Ir $5d^76s^2$ 192,22	78 Pt $5d^96s^1$ 195,09	79 Au $5d^{10}6s^1$ 196,966	80 Hg $5d^{10}6s^2$ 200,59	81 Tl $6s^26p^1$ 204,37	82 Pb $6s^26p^2$ 207,2	83 Bi $6s^26p^3$ 208,9804	84 Po $6s^26p^4$ [209]	85 At $6s^26p^5$ [210]	86 Rn $6s^26p^6$ [222]
103 (Lr) $5f^{14}6d^17s^2$ [260]	104 (Ku) $6d^27s^2$ [261]	105 (Ns) [261]	106 [263]	107 [261]	108	109	110	111	112	113	114	115	116	117	118

Н. С. АХМЕТОВ

ОБЩАЯ И НЕОРГАНИЧЕСКАЯ ХИМИЯ

ИЗДАТЕЛЬСТВО «ВЫСШАЯ ШКОЛА»
МОСКВА

N. S. AKHMETOV

General and Inorganic Chemistry

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by
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(c) English translation, Mir Publishers, 1983

It is only through theory that our knowledge is moulded into a whole and becomes scientific knowledge; science is the orderly combination of factual knowledge and theory.

A. M. Butlerov

PREFACE TO THE ENGLISH EDITION

This textbook is intended for first-year chemistry students. Its scope, subject matter, and method of presentation of the material assume that the student has already studied the main concepts of chemistry, its most important laws, and the properties of the elements and their most important compounds at school.

The text consists of two parts. Part One describes the main theoretical concepts on which chemical science is based, and surveys the periodic law and structure of atoms, chemical bonds and the structure of matter, the thermodynamic and kinetic laws of processes, and types of chemical reactions.

Part Two includes the factual data of inorganic chemistry with special emphasis on exposition of the main patterns and properties of elements and compounds stemming from the position of the elements in the Mendeleev's periodic system.

The student can acquire comprehensive knowledge only provided he or she has mastered the concrete concepts of the main substances and interconversions studied, which depends, to a considerable extent, on independent hard work in the laboratory and solution of problems and exercises (see N. Akhmetov, M. Azizova, and L. Badygina, *Problems and Laboratory Experiments in Inorganic Chemistry*, Mir Publishers, Moscow, 1982). Unity of the aims and tasks of

laboratory practice and seminar subjects should, in our opinion, prepare the student for real research. 'From living observation to abstract thought *and from that to practice*,—such is the dialectical path of the cognition of truth, of the cognition of objective reality.' (V. I. Lenin, *Philosophical Notebooks*, p. 171)

I take this opportunity to express my thanks to the staff of Mir Publishers for their thoughtful, careful translation and preparation of my book for publication in English.

Nahil Akhmetov
Kazan

CONTENTS

Part One. INTRODUCTION TO INORGANIC CHEMISTRY 13

I. The Periodic Law and the Structure of the Atom 15

Chapter 1. The Electron Shells of Atoms 18
1.1. The Principles of Quantum Mechanics 18
1.2. Electron Clouds 20
1.3. Atomic Orbitals 23

Chapter 2. Mendeleev's Periodic System as the Natural Classification of Elements by the Electron Structure of Atoms 29
2.1. The Electron Structure of Atoms 29
2.2. Structure of the Periodic System 37

Chapter 3. The Periodicity of the Properties of Elements 39
3.1. Energy of Ionisation. Electron Affinity. Electronegativity 39
3.2. Radii of Atoms and Ions 46
3.3. Secondary Periodicity 48

II. The Chemical Bond 50

Chapter 1. Fundamental Notions of the Chemical Bond 51
1.1. Certain Parameters of a Molecule 51
1.2. The Nature of the Chemical Bond 52
1.3. The Curve of Potential Energy for a Molecule 54

Chapter 2. Molecular Orbital Theory 55
2.1. Molecular Orbitals 55
2.2. Diatomic Homonuclear Molecules 58
2.3. Diatomic Heteronuclear Molecules 65
2.4. Triatomic Linear Molecules 66
2.5. Pentatomic Tetrahedral Molecules 71
2.6. Comparison of the Energy Diagrams of Different Molecular Orbitals 73

Chapter 3. The Theory of Valence Bonds 74
3.1. The Saturation of Covalent Bonds 74
3.2. Direction of a Covalent Bond 77
3.3. The Polarity and Polarisability of Bonds 88
3.4. Types of Covalent Molecules 90

Chapter 4. Ionic Bonds. Nonvalent Types of Bonds 94
4.1. Ionic Bonds 94
4.2. Metallic Bonds 96
4.3. Interactions Between Molecules 97
4.4. Hydrogen Bonds 99

Chapter 5. Complex Formation. Complex Compounds 101
5.1. Complex Formation 101
5.2. Complex Compounds 101
5.3. Complex Compounds from the Standpoint of Valence Bond Theory 104

III. States of Aggregation. Dispersed Systems 106

Chapter 1. The Solid State 106
1.1. Crystals 106
1.2. Types of Chemical Bond in Crystals 108
1.3. The Principal Structural Types of Inorganic Substances 110
1.4. The Characteristic Coordination Number of Elements and Structure of Their Compounds 119
1.5. The Band Theory of Crystals 122
1.6. Semiconductors 124

Chapter 2. The Liquid State 126
2.1. The Structure of Liquids 126
2.2. Ionisation of the Molecules of Liquids 127
2.3. The Amorphous State 129

Chapter 3. The Gaseous and Other States of Matter 129
3.1. The Gaseous State 129
3.2. Plasma 130
3.3. Other States of Matter 131

Chapter 4. Dispersed Systems 132
4.1. Solutions 132
4.2. Gaseous Solutions 133
4.3. Liquid Solutions 134
4.4. Solid Solutions 141
4.5. Eutectic Mixtures 142

Chapter 5. Physicochemical Analysis 142
5.1. Thermal Analysis 142
5.2. Types of Phase Diagram 143

IV. Methods of Investigating the Structure of Substances 147

Chapter 1. Spectroscopic Methods 147
1.1. The Electromagnetic Spectrum and Atomic or Molecular Processes 147
1.2. X ray Spectroscopy 148
1.3. Optical Spectroscopy 150

1.4. Radiospectroscopy 154
1.5. Gamma-ray Spectroscopy 155
Chapter 2. Diffraction Analysis 158
2.1. X-ray Crystallography 158
2.2. Electron and Neutron Diffraction Analysis 160
Chapter 3. Study of the Behaviour of Substances in Magnetic and Electric Fields 162
3.1. Magnetic Measurements 162
3.2. Study of Dipole Moments 164
V. Introduction to the Theory of Chemical Processes 166
Chapter 1. The Energy Relations of Chemical Conversions 167
1.1 Heat of Reaction 167
1.2. Thermochemical Equations 168
Chapter 2. Direction of Chemical Reactions 177
2.1. Entropy 177
2.2. Gibbs' Free Energy 180
Chapter 3. Chemical Equilibrium 184
3.1. Equilibrium Constant 184
3.2. Le Chatelier's Principle 187
3.3. Ionisation Constant 189
3.4. The Stability Constant of Complex Compounds 193
3.5. Autoprotolysis Constant 195
3.6. Equilibrium in Heterogeneous Systems 196
Chapter 4. Chemical Kinetics 198
4.1. Velocity of Chemical Reaction 198
4.2. Activation Energy 202
4.3. The Mechanism of Chemical Reactions 205
4.4. Physical Stimulation of Chemical Conversions 208
4.5. Catalysis 211
Chapter 5. Reactions Without Change of the Elements' Oxidation State 213
5.1. Conditions for One-way Reactions 213
5.2. Hydrolysis 215
Chapter 6. Reactions with Alteration of Oxidation State 221
6.1. Oxidation-reduction Reactions 221
6.2. Balancing the Equations of Redox Reactions 221
6.3. Direction of Redox Reactions 225
6.4. Chemical Sources of Electricity 229
Part Two. SURVEY OF THE ELEMENTS AND MOST IMPORTANT CHEMICAL COMPOUNDS 232
I. Introduction to the Chemistry of the Elements 232
Chapter 1. The Abundance of Chemical Elements 232
1.1. Geochemistry and Cosmochemistry 232

1.2. The Abundance of Chemical Elements in the Universe 233
1.3. Chemical Elements in the Earth's Crust 234

Chapter 2. Simple Substances 239
2.1. The Structure of Simple Substances 239
2.2. Properties of Simple Substances 242
2.3. Preparation of Simple Substances 248

Chapter 3. Binary Compounds 253
3.1. Characteristics of Binary Compounds by Type of Bond 253
3.2. Comparison of the Stability of Binary Compounds 256
3.3. The Acid-Base Properties of Binary Compounds 257
3.4. Intermetallic Compounds 259

Chapter 4. Ternary Compounds 263
4.1. Derivatives of Anion Complexes 263
4.2. Mixed Compounds, Solid Solutions, Eutectics 265

Chapter 5. Nonstoichiometric Compounds 267
5.1. Compounds of Variable Composition 267
5.2. Inclusion Compounds 268

II. The Chemistry of *s* and *p* Elements 270

Chapter 1. General Patterns 270
1.1. Oxidation States of *s* and *p* Elements 271
1.2. Coordination Numbers of *s* and *p* Elements 273

Chapter 2. Hydrogen 277

Chapter 3. Group VII *p* Elements 286
3.1. Fluorine 286
3.2. Chlorine 291
3.3. Bromine Subgroup 303

Chapter 4. Group VI *p* Elements 313
4.1. Oxygen 314
4.2. Sulphur 326
4.3. The Selenium Subgroup 340

Chapter 5. Group V *p* Elements 347
5.1. Nitrogen 348
5.2. Phosphorus 368
5.3. The Arsenic Subgroup 383

Chapter 6. Group IV *p* Elements 393
6.1. Carbon 394
6.2. Silicon 412
6.3. Germanium Subgroup 424
6.4. Oxycompounds of the *p* Elements of Group IV, V, VI and VII 433

Chapter 7. Group III *p* Elements 437
7.1. Boron 437
7.2. Aluminium 452

7.3. Gallium Subgroup 463
Chapter 8. Group II *s* Elements 471
8.1. Beryllium 472
8.2. Magnesium 477
8.3. Calcium Subgroup 481
Chapter 9. Group I *s* Elements 486
9.1. Lithium 487
9.2. Sodium 490
9.3. Potassium Subgroup 492
Chapter 10. Group VIII *s* and *p* Elements 495
10.1. Helium 496
10.2. Neon 497
10.3. Argon 497
10.4. The Krypton Subgroup 498
III. The Chemistry of *d* Elements 504
Chapter 1. General Features 504
1.1. Oxidation States of *d* Elements 504
1.2. Coordination Compounds of *d* Elements 505
1.3. Description of Complex Compounds by Crystal Field Theory 505
1.4. Description of Complex Compounds by Molecular Orbital Theory 511
1.5. Electron Configuration of Complexing Agents and Structure of Complexes 519
1.6. Complexes with Organic Unsaturated Molecules and Ions as Ligands 520
1.7. Isomerism of Complex Compounds 522
Chapter 2. Group III *d* Elements 524
2.1. Scandium Subgroup 526
2.2. Compounds of the Scandium Subgroup Elements 526
Chapter 3. Group IV *d* Elements 528
3.1. Titanium Subgroup 529
3.2. Compounds of the Titanium Subgroup Elements 531
Chapter 4. Group V *d* Elements 538
4.1. Vanadium Subgroup 540
4.2. Compounds of the Vanadium Subgroup Elements 541
Chapter 5. Group VI *d* Elements 548
5.1. Chromium Subgroup 549
5.2. Compounds of the Chromium Subgroup Elements 551
Chapter 6. Group VII *d* Elements 567
6.1. Manganese Subgroup 568
6.2. Compounds of the Manganese Subgroup Elements 570
Chapter 7. Group VIII *d* Elements 578
7.1. Iron Subgroup 579
7.2. Compounds of the Iron Subgroup Elements 581

7.3. The Cobalt Subgroup 592
7.4. Compounds of the Cobalt Subgroup Elements 595
7.5. The Nickel Subgroup 604
7.6. Compounds of the Nickel Subgroup Elements 606
7.7. The Refining of Platinum Metals 616

Chapter 8. Group I *d* Elements 617
8.1. The Copper Subgroup 619
8.2. Compounds of the Copper Subgroup Elements 621

Chapter 9. Group II *d* Elements 628
9.1. The Zinc Subgroup 629
9.2. Compounds of the Zinc Subgroup Elements 631

IV. The Chemistry of *f* Elements 636

Chapter 1. Sixth Period *f* Elements 636
1.1. The Lanthanides 636
1.2. Compounds of the Lanthanides 641

Chapter 2. Seventh Period *f* Elements 644
2.1. The Actinide Family 647
2.2. Compounds of Actinides 648

V. Transmutation of Chemical Elements 654

Chapter 1. Radioactivity 654
1.1. Nuclear Fission 654
1.2. Radioactive Series 655

Chapter 2. Nuclear Reactions 657
2.1. Synthesis of Elements 659
2.2. The Outlook for the Synthesis of New Elements 661
2.3. Nuclear Reactions in Nature 661

Selected Readings 663

Index

PART ONE

INTRODUCTION TO INORGANIC CHEMISTRY

> The human conception of cause and effect always somewhat simplified the objective connection of the phenomena of nature.
>
> V. I. Lenin. *Materialism and Empiriocriticism*

Chemistry is one of the natural sciences that study the material world in all the variety of its existence and transformations.

Matter exists, as objective reality, in two forms: viz., *substance* and *field*. These forms are closely interconnected, displaying in their interconversions the deep inner contradictions that are a necessary attribute of any objective existence. By *substance* we mean that form of the existence of matter in which it appears primarily as particles possessing mass proper (i.e. rest mass). It is matter in its various stages of organisation, viz., elementary particles (electrons, protons, neutrons), atomic nuclei, atoms, molecules, molecular aggregations (crystals, liquids, gases), minerals, rocks, vegetable and animal tissues, and so on. A *field* (gravitational, electromagnetic, intranuclear, etc.) is the form of existence of matter that is primarily characterised by, and manifests, energy rather than mass, although it also possesses the latter.

Modern views of matter reflect its *discreteness*, since any body or field is composed of 'elementary' bodies or 'elementary' fields, known as *microparticles* and *microfields*. The whole diversity of macroobjects (substances and fields) arises from the variety of possible combinations of a limited number (several dozen) of qualitatively different microobjects, e.g. electrons, positrons, protons, neutrons, etc.

In Frederick Engels' definition, 'the subject of natural science is moving matter, bodies'.* Hence each natural science studies a separate form of the motion of matter.

---

* Letter to Karl Marx, 30 May 1873. Karl Marx, Friedrich Engels. *Werke*, Vol 33 (Dietz Verlag, Berlin, 1973), p. 80.

At each particular stage of its organisation, matter has its own inherent form of motion. For example, the interaction and conversion of protons and neutrons and formation of atomic nuclei is the nuclear form of motion; the chemical form of motion of matter corresponds to the interaction of atoms and formation of molecules, and so on.

Definite sciences study the different stages of the organisation of matter and the specific forms of motion inherent in them. Elementary particles, for instance, and their transformations and interactions are studied by the physics of elementary particles; the processes of the formation and destruction of rocks are studied by geology, and the processes of vital activity by biology, and so on.

It must not be thought, of course, that there is an unequivocal strict correlation between the sciences on the one hand, and the forms of motion of matter on the other. It must be remembered that there is no form of the motion of matter at all that could exist in pure form independent of the other forms of motion. That is what makes it difficult to classify the sciences.

Chemistry can be defined as *the science that studies substances and the processes of their interconversions associated with changes in their composition and structure.*

A chemical process is accompanied with a change in the composition and structure of substances, and necessarily with energy changes in the reacting system. In a chemical process there is a regrouping of atoms that is accompanied with the breaking of chemical bonds in the initial substances and formation of chemical bonds in the reaction products. Because of the interconnections between the forms of motion of matter and their interconversions during chemical reactions, chemical energy is converted into heat, light, etc.

Man needs chemistry in order to obtain all the things he needs from the substances of nature, viz., metals, cement and concrete, ceramics, porcelain and glass, rubber, plastics, man-made fibres, and pharmaceutical preparations.

The Nobel Prize winner N. N. Semyonov therefore defines the subject matter of chemistry both as a science and as an industry as the obtaining of new substances (products) possessing quite different properties from certain initial substances (raw materials).

Modern chemistry is a system of separate scientific disciplines (general, inorganic, analytical, organic, physical, and colloid chemistry; biochemistry, geochemistry, space chemistry, electrochemistry, etc.). The basis of chemical science is the theory of atoms and molecules, the law of the conservation of matter, the periodic law, and the theory of structure.

I

THE PERIODIC LAW AND THE STRUCTURE OF THE ATOM

> The properties of simple and complex bodies depend in a periodic way on the atomic weight of the elements simply because these properties are themselves the result of the properties of the elements forming the bodies.
>
> D. I. Mendeleev

The modern view of elements became possible only after Mendeleev's discovery of the periodic law (1869).

The definition of an element that he gave is very close to the modern one:

> By the term element is to be understood those material constituents of simple and complex bodies that lend them a certain set of physical and chemical properties. Just as the concept of a particle corresponds to a simple body, so element corresponds to the concept of an atom.

A chemical element is a type of atom characterised by a definite nuclear charge.

The periodic system is an expression of the periodic law. It brings out the profound link between all chemical elements and shows that, being governed by a single law, they are single in nature. The interconnection between them is expressed, for example, in the fact that their properties can be roughly predicted (as Mendeleev himself did).

The discovery of the periodic law and periodic system of elements completed the development of atomistic ideas in the nineteenth century. For all their immense importance, however, they were then only a brilliant empirical generalisation of the facts; their physical sense and profound essence remained undisclosed for a long time. The discovery of the periodic law prepared the ground for the onset of a new stage, study of the structure of atoms, and that in turn provided grounds for a deeper insight into the nature of the interconnections and qualitative differences between elements and an explanation of the regularities in the periodic system.

Ernest Rutherford, who developed the planetary model of the atom (1911), and Niels Bohr, who advanced the first quantum theory

of the atom (1913), played a special role in the development of today's theory of atomic structure.

The atom is a complicated microsystem consisting of moving elementary particles. It consists of a positively charged *nucleus* and negatively charged *electrons*. The carrier of the nucleus's positive charge is the *proton*. The nuclei of all elements, except the light isotope of hydrogen, also contain *neutrons*. The main characteristics of the electron, proton, and neutron are given in Table 1.

Table 1. **Data on Selected Elementary Particles**

Particle	Symbol	Rest mass		Charge, C
		kg	atomic mass units	
Proton	p	1.673×10^{-27}	1.007276	1.602×10^{-19}
Neutron	n	1.675×10^{-27}	1.008665	0
Electron	e	1.108×10^{-31}	1.000549	1.602×10^{-19}

The nucleus is the fundamental basis of the atom and determines the individuality of the elements.

The radii of atoms vary from 0.05 nm to 0.30 nm. The mass of an atom m can be determined by dividing the molar mass of the element concerned M by the number of atoms in a mole*: $m = M/N_A$, where N_A is *Avogadro's constant*:

$$N_A \approx 6.02 \times 10^{23} \text{ mole}^{-1}$$

The mass of the atoms of various elements varies from $1.67 \times \times 10^{-27}$ kg to 4.27×10^{-25} kg.

The absolute mass of an atom is very small; it is therefore expressed in *atomic mass units*. The atomic mass unit is taken at present as 1/12 of the mass of the atom of the carbon isotope $^{12}_{6}C$.

As can be seen from Table 1, the mass of an electron is about 1/1840 of that of a proton and neutron. The mass of an atom is therefore practically equal to the mass of the nucleus, i.e. the sum of the masses of its nucleons (protons and neutrons).

The properties of a nucleus depend in the main on its composition, i.e. on the number of protons and neutrons. The number of protons in the nucleus determines the charge of the nucleus and identifies

* The mole is a basic SI unit. It describes the quantity of a substance in a system containing the same number of structural elements as the number of atoms contained in a nuclide of $^{12}_{6}C$ with a mass of 0.012 kg. The structural elements can be atoms, ions, molecules, electrons, and other particles or groups of particles.

the atom as belonging to a given element. Another important characteristic is the mass number A of the nucleus, which is equal to the total number of protons Z and neutrons N in it:

$$A = Z + N$$

Atoms with a different number of protons (Z) and neutrons (N) but with the same number of nucleons (A) are known as *isobars*. Atoms with the same number of protons (Z) are called *isotopes* and those containing the same number of neutrons (N) are *isotones*. Examples of isotopes, isobars, and isotones are given below.*

Isotopes	*Isobars*	*Isotones*
$^{40}_{20}$Ca	$^{40}_{18}$Ar	$^{136}_{54}$Xe
(20p, 20n)	(18p, 22n)	(54p, 82n)
$^{42}_{20}$Ca	$^{40}_{19}$K	$^{138}_{56}$Ba
(20p, 22n)	(19p, 21n)	(56p, 82n)
$^{43}_{20}$Ca	$^{40}_{20}$Ca	$^{139}_{57}$La
(20p, 23n)	(20p, 20n)	(57p, 82n)

Comparison shows that the mass of a nucleus is always *less* than the arithmetical sum of the masses of its protons and neutrons. The difference is known as the *mass defect*. The mass of the nucleus of the $^{4}_{2}$He (2p, 2n) isotope, for instance, is 4.001506 amu, but the sum of the masses of the two protons and two neutrons is 4.031882 amu ($2 \times 1.007276 + 2 \times 1.008665$), i.e. the mass defect is 0.030376 amu.

Mass defect characterises the stability of atomic nuclei and the binding energy of their nucleons. It corresponds to the energy that is liberated when a nucleus is formed from free protons and neutrons, and can be calculated from Einstein's mass-energy equation

$$E = mc^2$$

where E is the energy, m the mass, and c the velocity of light in a vacuum ($c = 3 \times 10^8$ m/s).

In accordance with this equation the reduction of mass by 0.030376 amu during the formation of a helium nucleus from two protons and two neutrons corresponds to the liberation of the enormous energy of 28.2 MeV (1 MeV$=10^6$ eV). Hence, its mean binding energy per nucleon is about 7 MeV. The binding energy of the nucleons in a nucleus is millions of times greater than that of the atoms in a molecule (about 5 eV). That is why nuclei are not altered in the chemical conversion of substances.

According to the current theory the atomic nucleus has a *shell structure*. Protons and neutrons, independently, fill the nuclear layers and sublayers in the same way as electrons are observed to fill an atom's electron shells.

At present, around 300 stable and more than 1400 radioactive nuclei are known. It has been established that nuclei with 2, 8, 14, 20, 28, 50, or 82 protons or neutrons and 126 or 152 neutrons differ markedly in their properties from other elements. It is suggested that these *magic numbers* of nucleons cor-

* The indices showing the mass and atomic number of an element (number of protons) are placed on the left of its chemical symbol, the superscript indicating the mass number and the subscript the nuclear charge.

respond to completely filled nuclear shells and subshells. The *magic number* of a nucleus may be (1) the number of protons, (2) the number of neutrons, or (3) the number of protons and neutrons ('double magic'). The double magic numbers include the nuclei of $^{4}_{2}$He (2p, 2n), $^{16}_{8}$O (8p, 8n), $^{28}_{14}$Si (14p, 14n), $^{40}_{20}$Ca (20p, 20n), and $^{208}_{82}$Pb (82p, 126n). $_{28}$Ni, $_{50}$Sn, and $_{82}$Pb have magic numbers of protons; $^{88}_{38}$Sr (38p, 50n) $^{90}_{40}$Zr (40p, 50n); and $^{138}_{56}$Ba (56p, 82n), $^{139}_{57}$La (57p, 82n), $^{140}_{58}$Ce (58p, 82n), etc., have magic numbers of neutrons.

CHAPTER 1

The Electron Shells of Atoms

1.1. The Principles of Quantum Mechanics

The modern theory of the structure of the atom is based on the laws describing the motion of microparticles (micro-objects). Since the mass and dimensions of microparticles are extremely small compared with those of macroscopic bodies, the properties and regularities of the motion of a separate microparticle differ qualitatively from those of the motion of a macroscopic body, which have long been described by classical physics. A new branch of physics, *quantum* (or *wave*) *mechanics*, arose in the 1920s that describes the motion and interaction of microparticles. It is based on the concepts of a quantum of energy, the wave character of the motion of microparticles, and the probability (statistical) method of describing micro-objects.

The quantum character of the emission and absorption of energy. Around the beginning of this century study of certain phenomena, such as the emission of hot objects, photoelectric effect, atomic spectra, led to the conclusion that energy is not propagated and transmitted, absorbed or emitted continuously but discretely, in separate portions or *quanta*. The energy of a system of microparticles also can have only certain values that are multiples of quanta; so the energy of such systems can only change by jumps, or be *quantised*.

The quantisation of energy was first postulated by Max Planck (1900), and was later substantiated by Albert Einstein (1905). The energy of a quantum ΔE depends on the frequency of the radiation ν:

$$\Delta E = h\nu \qquad (1)$$

where h is *Planck's constant* (6.63×10^{-34} J·s).

Frequency and wavelength are linked by the relationship $\lambda\nu = c$, where c is the velocity of light (3×10^{8} m/s).

In accordance with equation (1), the shorter the wavelength (i.e. the higher the frequency), the greater is the energy of a quantum, and vice versa, the longer the wavelength (i.e. the lower the frequency), the lower the energy of a quantum. Ultraviolet rays and

X-rays, for example, therefore have higher energies than radio waves or infra-red rays.

The wave nature of the motion of microparticles. Both wave and corpuscular concepts are used to describe electromagnetic radiation. On the one hand monochromatic radiation is propagated as a wave and has a wavelength λ (or frequency ν); on the other hand it consists of microparticles or *photons* that carry quanta of energy. The diffraction and interference of electromagnetic radiation (light, radio waves, gamma rays, X-rays, etc.) are convincing proof of its wave nature. At the same time it possesses energy and mass, exerts pressure, and so on. (It is calculated that the mass of the Sun, for instance, diminishes annually through radiation by 1.5×10^{17} kilograms.)

In 1924, Louis de Broglie suggested extending the corpuscular/wave concepts to all microparticles, i.e. that the motion of any microparticle be regarded as a wave process. Mathematically this is expressed by the *de Broglie equation*, according to which a particle of mass m moving at a velocity v has a certain wavelength λ:

$$\lambda = h/mv \tag{2}$$

De Broglie's hypothesis was proved experimentally by the discovery of diffraction and interference effects in a stream of electrons. Today the diffraction of streams of electrons, neutrons, and protons is widely used to study the structure of matter (see IV).

According to equation (2) the motion of an electron (mass 9.1×10^{-31} kg, velocity of the order of 10^6 m/s) is associated with a wavelength of the order of 10^{-10} metres, i.e. the wavelength is commensurate with the atom's size. When a beam of electrons is scattered by a crystal, diffraction is observed, the crystal acting as a diffraction lattice. The motion of macroparticles is associated, on the contrary, with such short wavelengths (10^{-29} m and less) that the wave process cannot be observed experimentally.

The uncertainty principle. Werner Heisenberg set forth the principle (1927) that *it is impossible to accurately determine both the position (or coordinates) and the amount of motion (or momentum* $p = mv$*) of a microparticle simultaneously*. The mathematical expression of the uncertainty principle is

$$\Delta x \, \Delta p \geqslant \frac{h}{2\pi} \quad \text{or} \quad \Delta x \, \Delta v \geqslant \frac{h}{2\pi m} \tag{3}$$

where Δx, Δp, Δv are uncertainties of position, momentum and velocity of a particle respectively.

It follows from equation (3) that the higher the accuracy of the determination of the coordinate of a particle (i.e. the lower the uncertainty of Δx), the less certain the value of its momentum and velocity will be (i.e. the higher Δp and Δv) and vice versa, the more

accurate the impulse (velocity), the less certain the position of the particle. Thus, if the position of an electron is determined with an accuracy of 10^{-12} m, the uncertainty of its velocity will be 58 000 km/s (the velocity of an electron being 2000 km/s).

The ratio h/m is very small (Δx and Δv tend to zero) for macroparticles (heavy particles) so that the laws of classical mechanics hold for them, and the position and velocity of a particle can be determined simultaneously within their context.

The quantisation of energy, wave nature of the motion of microparticles, and the uncertainty principle all indicate that classical mechanics is quite unsuitable for describing the behaviour of microparticles. The state of an electron in an atom thus cannot be represented as the motion of a material particle along an orbit. Quantum mechanics does not locate the position of an electron accurately in space but replaces the classical concept of a particle's precise position by the idea of a statistical *probability* of its being at a definite point in space or in an element of volume dV around the nucleus.

1.2. Electron Clouds

Wave function. Since the motion of an electron has a wave character, quantum mechanics describes its motion in an atom by what is called a *wave function* ψ. This function is different for various points of atomic space. Mathematically it is written as the equality $\psi = \psi(x, y, z)$, where x, y, z are the coordinates of a point. The physical sense of a wave function is that its square ψ^2 characterises the probability of the electron concerned being at a definite point in atomic space. The value $\psi^2 dV$ is the probability of the particle in question being in an element of volume dV.

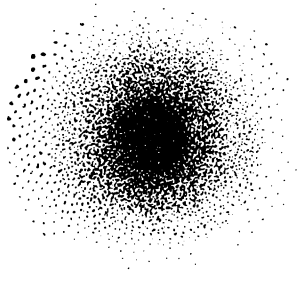


Fig. 1. An electron cloud

The model of an electron in an atom accepted in quantum mechanics is the idea of an *electron cloud*, the density of the corresponding sections of which is proportional to the probability of the presence in it of an electron. A possible form of the electron cloud in an atom is shown in Fig. 1.

This figure can be interpreted as follows. Let us assume that we have photographed the position of an electron at some moment of time in the three-dimensional space around the nucleus, and that this is shown on the photographs as a dot. Repeat the determination thousands of times. The new photographs taken at short intervals will discover the electron in new positions. When all the photographs

are superimposed on one another, they will yield a picture resembling a cloud. The cloud will be densest, obviously, where the number of dots is greatest, i.e. where the probability of the electron's being in the cloud is highest.

The stronger the bond between the nucleus and the electron, obviously, the smaller the electron cloud will be and the denser the distribution of the charge. An electron cloud is often depicted as a *boundary surface* (containing about 90 per cent of it). Density is then no longer described by dots (Fig. 2). The space around the nucleus in which the probability of finding the electron is highest is called the *orbital.** The configuration and size of the boundary surface would usually be regarded as the shape and size of the orbital (electron cloud).

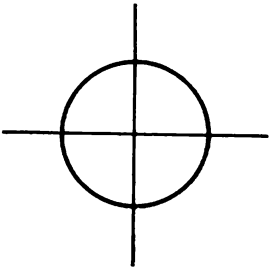


Fig. 2. Section of boundary surface

It is a complicated mathematical problem to calculate the probability of an electron's being at a given spot of an atom (molecule), and of measuring its energy. It is solved by means of the *Schrödinger equation.*

The Schrödinger wave equation. In 1926 Erwin Schrödinger proposed his wave equation. It determines the change in the wave function in space depending on the field of force in which the electron moves.

The Schrödinger equation links the wave function ψ with an electron's potential energy U and its full energy E:

$$\frac{h^2}{8\pi^2 m} \nabla^2\psi + (E-U)\,\psi = 0$$

The first term of the equation corresponds to kinetic energy of an electron. Here $\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$ is the sum of the second derivatives of the wave function ψ along the coordinates x, y, and z; m is the electron's mass; and h is Planck's constant.

Without going into the mathematical sense of the wave function, let us note that acceptable solutions can only be obtained with quite definite, discrete values of the electron's energy. The various functions ψ_1, ψ_2, ψ_3, . . ., ψ_n that are solutions of the wave equation correspond to energies E_1, E_2, . . ., E_n respectively. Quantisation of the energy of a microsystem thus stems directly from solution of the wave function.

A wave function that is a solution of the Schrödinger equation is called an *orbital.*

* This interpretation of the orbital is rather simplified. An orbital is a mathematical concept whose sense stems from the wave equation.

The variation of ψ and ψ^2 for the electron of the hydrogen atom at a distance r from the nucleus, in accordance with its various energy states, is shown in Figs. 3 and 4. The curve in Fig. 3 describes the state of an electron possessing minimum energy. The shape of the ψ

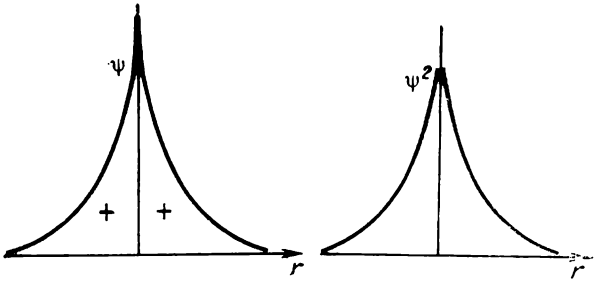


Fig. 3. Curves for ψ and ψ^2 for the electron of a hydrogen atom with minimum energy

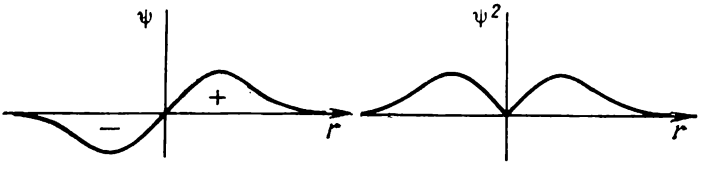


Fig. 4. Curves for ψ and ψ^2 for the electron of a hydrogen atom in an excited state

and ψ^2 curves corresponds to an electron cloud with spherical symmetry (Figs. 1 and 2). In whatever direction the values of r are plotted, ψ^2 decreases uniformly. It will also be seen that the ψ curve lies to one side of the spacing axis (y-axis), which indicates that the wave function has a certain sign (let us assume it to be positive).

When a hydrogen atom absorbs energy, its electron state is altered, which entails a corresponding change in the configuration of the curves (see Fig. 4), so that the wave function is now positive on one side of the nucleus and negative on the other, while the value of ψ becomes zero at the point of intersection of the coordinates (ψ^2, of course, is always positive.) The arrangement and configuration of the curves in Fig. 4 show that the wave function and its square are not, in this case, spherically symmetrical. The electron cloud is concentrated along the x-axis, while the probability of finding an electron in the yz plane perpendicular to this axis is zero. Such an electron cloud has a dumb-bell shape (see Fig. 7).

1.3. Atomic Orbitals

Quantum numbers. An orbital can be described definitely by a set of integral numbers known as *quantum numbers*. These are depicted as follows: n, the principal quantum number; l, the orbital angular (azimuthal) quantum number; and m_l, the magnetic orbital quantum number.

The principal quantum number. Energy levels. In accordance with the principles of quantisation an electron can be only in definite *quantum states* in an atom that correspond to definite values of its binding energy. The wave functions found by solving the wave equation for the hydrogen atom, for instance, correspond only to those energies that are given by the formula

$$E = -\frac{2\pi^2 me^4}{n^2h^2} \text{ or } E = -13.6\,\frac{1}{n^2} \text{ eV}$$

where m is the electron's mass, e is its charge, h is Planck's constant, and n is any whole number from 1 to ∞, known as the *principal quantum number* ($n = 1, 2, 3, \ldots, \infty$).

The transition of an electron from one quantum state to another is associated with a jump in its energy. The energy of the quantum states and quantum transitions of electrons can be depicted graphically by a diagram of its energy levels (Fig. 5). The horizontal lines in the diagram are drawn at heights proportional to the electron's energies in the atom; the vertical lines indicate possible quantum transitions.

The quantum state of an atom with the lowest energy E_1 is known as the *normal* or *ground state*. Other states, with higher energies E_2, E_3, E_4, . . ., are known as *excited states*. An electron in the ground state is bound most firmly with the nucleus. When the atom is in an excited state this bond is weakened until the electron is stripped from it at E_∞.

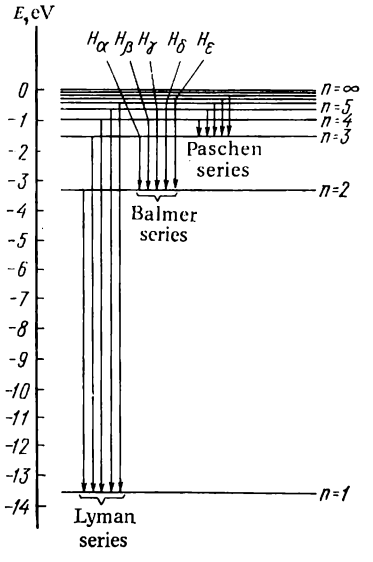


Fig. 5. Diagram of the energy levels and quantum transitions of the electron of a hydrogen atom

An atom can exist in the ground state for an unlimited time, but in an excited state for only a fraction of a second (10^{-8}-10^{-10} s).

An atom can be excited by heating, an electric discharge, absorption of light, etc., but however it is excited, it absorbs only certain

portions, or quanta, of energy corresponding to the difference between the energy levels of its electrons. The transfer of the electron of a hydrogen atom from level E_2 to level E_3, for example, requires the absorption of 1.89 eV of energy. The reverse transition is accompanied with the emission of exactly the same portion of energy.

The quantum transitions of an electron correspond to a jump in the average size of the electron cloud: a decrease in its binding energy corresponds to an increase in the volume of the electron cloud, while an increase leads to a contraction of the cloud.

Atomic spectra. The quantisation of atoms' energy is shown experimentally in their emission and absorption spectra. Atomic spectra are *linear* (Fig. 6). Spectral lines arise as follows: when atoms are excited (by heating of a gas, or by an electric discharge, etc.), their electrons accept appropriate portions of energy and pass to states with higher energy levels. The excited state lasts for only an instance.

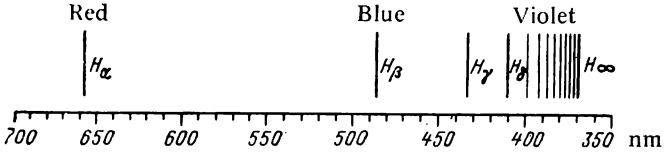


Fig. 6. Visible spectrum of atomic hydrogen (Balmer series)

The electrons' transition to states with lower energy levels is accompanied with the emission of quanta of energy according to the fundamental equation $\Delta E = h\nu$, which corresponds to the appearance of definite lines in the spectrum corresponding to a definite frequency (wavelength). Since gaseous atomic hydrogen contains many atoms at various levels of excitation, its spectrum consists of a great many lines. The quantum transitions of excited electrons from various levels to the ground state (see Fig. 5) correspond to the group of lines in the ultraviolet region of the spectrum (the *Lyman series*); their transitions to the second level correspond mainly to the visible region of the spectrum (the *Balmer series*); other transition series are expressed in the long-wave region of the spectrum. The visible spectrum of hydrogen (see Fig. 6) arises from the transition of excited electrons to a state with a principal quantum number $n = 2$.

The orbital quantum number. The configuration of orbitals. The *orbital* (or *azimuthal*) quantum number l is used to characterise the shape of an orbital, and hence the configuration of the electron cloud. This quantum number has values of 0, 1, 2, 3, . . ., $(n - 1)$. It corresponds to the orbital angular momentum of a quantity of an electron's motion

$$M = \frac{h}{2\pi} \sqrt{l(l+1)}$$

The orbital quantum number l is usually designated by letters as follows:

Orbital quantum number l	0	1	2	3	4	5
Designation	*s*	*p*	*d*	*f*	*g*	*h*

For each value of n the orbital quantum number l has definite values between 0 and $(n - 1)$:

Principal quantum number n	*Orbital (azimuthal) quantum number l*	*Orbital designation (of electron cloud)*
1	0	1*s*
2	0, 1	2*s*, 2*p*
3	0, 1, 2	3*s*, 3*p*, 3*d*
4	0, 1, 2, 3	4*s*, 4*p*, 4*d*, 4*f*

Thus only one orbital configuration is possible for an electron at the first energy level ($n = 1$); two orbital shapes are possible for the second energy level ($n = 2$); three for the third energy level ($n = 3$), and so on.

According to quantum-mechanical calculations, *s* orbitals are spherical, *p* orbitals have a dumb-bell shape, while *d*, *f*, and further orbitals are even more complicated. The shapes of *s*, *p*, and *d* boundary surfaces are shown in Fig. 7.* The sign of the wave function is also often indicated on drawings of the boundary surface. It should be remembered that the signs "+" and "—" do not refer to the probability of finding an electron ψ^2 (since it is always positive!) but refer to the wave function ψ which has different signs in different parts of the orbital (see Fig. 4).

In order to designate an electron's state, the principal quantum number is placed before the symbol of the orbital quantum number, e.g. 4*s* designates an electron for which $n = 4$, $l = 0$ (the cloud having the shape of a sphere); 2*p* designates an electron for which $n = 2$, $l = 1$ (the cloud having the shape of a dumb-bell), and so on.

The magnetic orbital quantum number. Spatial orientation of orbitals. A third quantum number m_l, known as the *magnetic quantum number*, is used to characterise the spatial distribution of orbitals (clouds). It has the following values: 0, ± 1, ± 2, ± 3, . . ., $\pm l$ and defines the value of the projection of the orbital momentum of the amount of motion with respect to a given direction (e.g. to the z axis):

$$M_z = \frac{h}{2\pi} m_l$$

* Since an orbital is described by the wave function ψ, and the distribution of its electron density by its square ψ^2, the shape of an orbital (except an *s* orbital) differs rather from that of the electron cloud.

The number of values of the magnetic quantum number depends on the orbital quantum number and indicates the number of orbitals with the given value of l (the number of which is $2l + 1$).

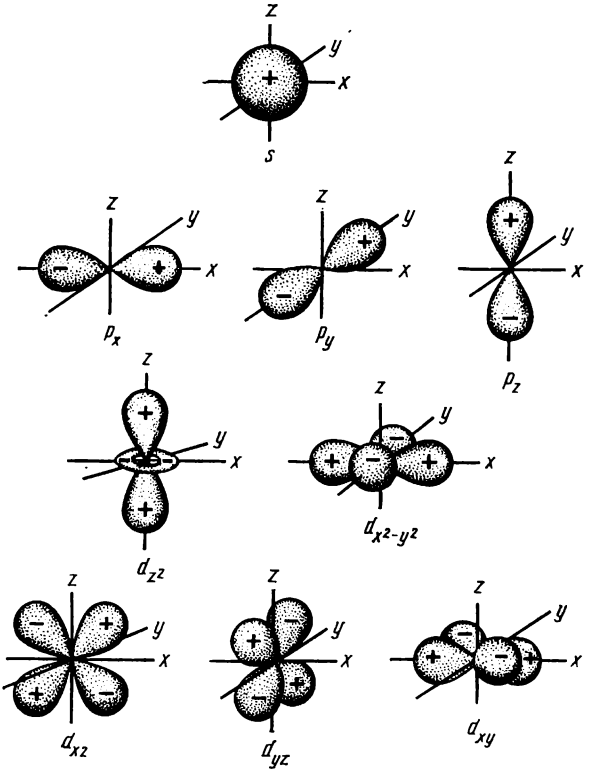


Fig. 7. Shapes of s, p, and d orbitals

Asimuthal quantum number l	*Magnetic quantum number* m_l	*Number of orbitals (clouds) with a given value of* l
0	0	1
1	1, 0, —1	3
2	2, 1, 0, —1, —2	5
3	3, 2, 1, 0, —1, —2, —3	7

One orbital corresponds to the s state, *three* to the p state, *five* to the d state, *seven* to the f state, and so on. Orbitals with identical energy are called *degenerate*; the p state is thus triply degenerate, the d state fivefold degenerate, and the f state sevenfold degenerate. The total number of orbitals at a given energy level is n^2.

Orbitals are designated as follows in accordance with their spatial orientation: p orbitals as p_x, p_y, and p_z; d orbitals oriented by their lobes along the coordinate axes as $d_{x^2-y^2}$, d_{z^2}, and d orbitals oriented between the coordinate axes as d_{xy}, d_{yz}, and d_{xz} (see Fig. 7).

The difference in electron clouds' orientation relative to one another explains the spectra of atoms in a magnetic field. In spectra placed in an external magnetic field there is a splitting of the lines to yield new, neighbouring ones, since the electrons' energy is altered in a magnetic field. The energy changes caused by the field is due to the difference in the character of the orientation of the electron clouds relative to one another (Fig. 7) and consequently to the different 'permissible' angles of rotation of each of them in the field.

Radial distribution of the electron density of orbitals. The distribution of electron densities in the space around the nucleus is also described by employing curves of the radial distribution of the probability (Fig. 8). The curves show the probability of the electron's being in a thin, concentric spherical layer with radius r and thickness dr around the nucleus. The volume of this layer is $dV = 4\pi r^2 dr$. The total probability of the electron's being in this layer is $(4\pi r^2\, dr)\, \psi^2$.

The radial distribution of electron density for the s, p, and d orbitals of the hydrogen atom is shown in Fig. 8*. It will be seen

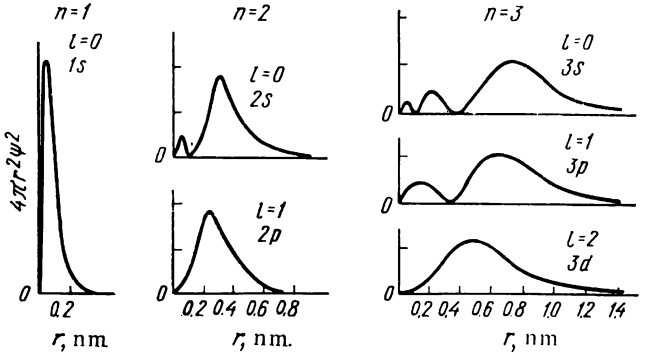


Fig. 8. Radial distribution of the probability of an electron (electron density) being at a distance r from the nucleus for a hydrogen atom

that the number of maxima on the distribution curve depends on the principal quantum number. Their number is the same as the principal quantum number n for s electrons, one less for p electrons, and two less for d electrons. Zero positions of ψ^2 are called *nodes* and correspond to a change of sign of the wave function ψ.

* Figure 8 describes the dependence of $4\pi r^2\psi^2$ on r.

Table 2. **Quantum States of Electrons, Filling Three Shells and Subshells**

Principal quantum number n	1	2				3								
Azimuthal quantum number l	0	0	1			0	1			2				
Magnetic orbital quantum number m_l	0	0	+1	0	−1	0	+1	0	−1	+2	+1	0	−1	−2
Magnetic spin quantum number m_s	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2	+1/2 −1/2
Orbitals	$1s$	$2s$	$2p_x$	$2p_z$	$2p_y$	$3s$	$3p_x$	$3p_z$	$3p_y$	$3d_{x^2-y^2}$	$3d_{xz}$	$3d_{z^2}$	$3d_{yz}$	$3d_{xy}$
Maximum number of electrons for a given value l (number of electrons in a subshell)	2	2	6			2	6			10				
Maximum number of electrons for a given value n (number of electrons in shell $2n^2$)	2	8				18								

Spin quantum number. Study of the fine structure of atomic spectra has shown that electrons are differentiated, in addition to differences in the size, shape, and orientation of their clouds (shells), by *spin*, which can be pictured in a simplified way as electrons' rotation about their own axes. A fourth quantum number, known as the *magnetic spin quantum number*, is introduced to characterise an electron's spin. It has two values: $+\frac{1}{2}$ and $-\frac{1}{2}$.

To summarise what has been said, the state of an electron in an atom can be described by four quantum numbers—n, l, m_l, and m_s—which characterise its energy, the volume and shape of the space around the nucleus within which it will probably be, and its spin. As an atom passes from one quantum state to another (in which connection the values of the quantum numbers change), the electron cloud is reconstructed, i.e. the atom absorbs or emits a quantum of energy.

Pauli's exclusion principle. In 1925 Wolfgang Pauli postulated that *no two electrons in an atom could have the same set of four quantum numbers.* In other words, given values of the quantum numbers n, l, m_l, and m_s can characterise only one electron. Any other electron in that atom must have at least one quantum number of different value.

It follows directly from Pauli's principle that two electrons can be present in one orbital, with $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$.

There can consequently be only two electrons in the s state (one orbital), six electrons in the p state (three orbitals), ten electrons in the d state (five orbitals), 14 electrons in the f state (seven orbitals), and so on.

Since each energy level includes n^2 orbitals, it can contain $2n^2$ electrons, i.e. the capacity of a level or subshell increases with distance from the nucleus and is 2 ($n = 1$), 8 ($n = 2$), 18 ($n = 3$), 32 ($n = 4$), etc., electrons (see Table 2).

CHAPTER 2

Mendeleev's Periodic System as the Natural Classification of Elements by the Electron Structure of Atoms

2.1. The Electron Structure of Atoms

The configuration of the electron shell of an unexcited atom depends on the charge of its nucleus. Electrons with the same principal quantum number n form a *quantum shell* of clouds of about the same

size. Shells with $n = 1, 2, 3, 4, \ldots$, are designated respectively by the letters K, L, M, N, . . ., P. As a shell's distance from the nucleus increases, the number of electrons it can accommodate also increases in accordance with the value of n: viz., 2 (shell K), 8 (shell L), 18 (shell M), 32 (shell N), etc. (see Table 2). Shells are built up in turn from subshells that accommodate electrons of the same value of l, or the orbital quantum number. Subshells consist of *orbitals*; each orbital can accommodate a maximum of two electrons (with opposite spins).

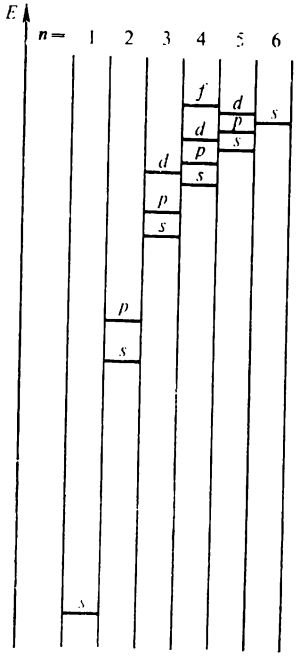


Fig. 9. Rough diagram of the energy levels in multielectron atoms

The most stable state of an atom is that in which the electrons are at the lowest energy level (i.e. in shells closest to the nucleus). The sequence of energy states in order of increasing energy of the orbitals of a multi-electron atom can be represented as follows: $1s < 2s < 2p < 3s < 3p < 4s \approx 3d < 4p < 5s \approx 4d < 5p < 6s \approx 5d \approx 4f < 6p$, etc. (see Fig. 9).

The order of the filling of the orbitals of a given subshell obeys the Hund rule that *the total spin number of the electrons of a given subshell must be maximal.*

In other words, the orbitals of a given subshell are first filled with one electron each, and then with a second. Electrons with opposite spins in the same orbital are paired and form a two-electron cloud with a total spin of zero.

The electron configurations of atoms in the ground state are given in Table 3.

The order of formation of electron shells of atoms can also be traced from the two versions of Mendeleev's periodic table given on inside covers.

The following symbols are commonly used when plotting the distribution of electrons in an atom: a line for an orbital; an arrow for an electron, the direction of the arrow indicating the orientation of the spin.

Short-period elements. The first period of the table consists of two elements. In the hydrogen atom the electron should be at the first energy level, i.e. the electron formula of an unexcited hydrogen atom is $1s^1$. Since s electron clouds are spheres, the structure of the

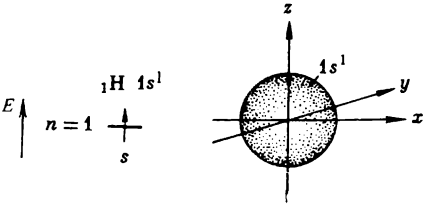
Table 3. **The Electron Configuration of the Elements**

Period	Z	Element	Electron configuration
1	1	H	$1s^1$
	2	He	$1s^2$
2	3	Li	[He] $2s^1$
	4	Be	$2s^2$
	5	B	$2s^22p^1$
	6	C	$2s^22p^2$
	7	N	$2s^22p^3$
	8	O	$2s^22p^4$
	9	F	$2s^22p^5$
	10	Ne	$2s^22p^6$
3	11	Na	[Ne] $3s^1$
	12	Mg	$3s^2$
	13	Al	$3s^23p^1$
	14	Si	$3s^23p^2$
	15	P	$3s^23p^3$
	16	S	$3s^23p^4$
	17	Cl	$3s^23p^5$
	18	Ar	$3s^23p^6$
4	19	K	[Ar] $4s^1$
	20	Ca	$4s^2$
	21	Sc	$3d^14s^2$
	22	Ti	$3d^24s^2$
	23	V	$3d^34s^2$
	24	Cr	$3d^54s^1$
	25	Mn	$3d^54s^2$
	26	Fe	$3d^64s^2$
	27	Co	$3d^74s^2$
	28	Ni	$3d^84s^2$
	29	Cu	$4d^{10}4s^1$
	30	Zn	$3d^{10}4s^2$
	31	Ga	$3d^{10}4s^24p^1$
	32	Ge	$3d^{10}4s^24p^2$
	33	As	$3d^{10}4s^24p^3$
	34	Se	$3d^{10}4s^24p^4$
	35	Br	$3d^{10}4s^24p^5$
	36	Kr	$3d^{10}4s^24p^6$
5	37	Rb	[Kr] $5s^1$
	38	Sr	$5s^2$
	39	Y	$4d^15s^2$
	40	Zr	$4d^25s^2$
	41	Nb	$4d^45s^1$
	42	Mo	$4d^55s^1$
	43	Tc	$4d^55s^2$
	44	Ru	$4d^75s^1$
	45	Rh	$4d^85s^1$
	46	Pd	$4d^{10}$
	47	Ag	$4d^{10}5s^1$
	48	Cd	$4d^{10}5s^2$
	49	In	$4d^{10}5s^25p^1$
	50	Sn	$4d^{10}5s^25p^2$
	51	Sb	$4d^{10}5s^25p^3$
	52	Te	$4d^{10}5s^25p^4$
	53	I	$4d^{10}5s^25p^5$
	54	Xe	$4d^{10}5s^25p^6$
6	55	Cs	[Xe] $6s^1$
	56	Ba	$6s^2$
	57	La	$5d^16s^2$
	58	Ce	$4f^26s^2$
	59	Pr	$4f^36s^2$
	60	Nd	$4f^46s^2$
	61	Pm	$4f^56s^2$
	62	Sm	$4f^66s^2$
	63	Eu	$4f^76s^2$
	64	Gd	$4f^75d^16s^2$
	65	Tb	$4f^96s^2$
	66	Dy	$4f^{10}6s^2$
	67	Ho	$4f^{11}6s^2$
	68	Er	$4f^{12}6s^2$
	69	Tm	$4f^{13}6s^2$
	70	Yb	$4f^{14}6s^2$
	71	Lu	$4f^{14}5d^16s^2$
	72	Hf	$5d^26s^2$
	73	Ta	$5d^36s^2$
	74	W	$5d^46s^2$
	75	Re	$5d^56s^2$

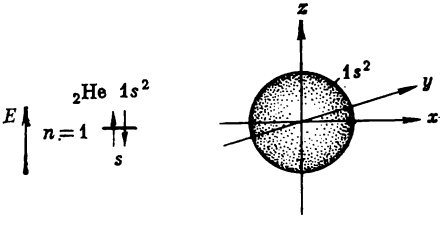
Table 3, continued

Period	Z	Element	Electron configuration	Period	Z	Element	Electron configuration
	76	Os	$5d^6 6s^2$		87	Fr	[Rn] $7s^1$
	77	Ir	$5d^7 6s^2$		88	Ra	$7s^2$
	78	Pt	$5d^9 6s^1$		89	Ac	$6d^1 7s^2$
	79	Au	$5d^{10} 6s^1$		90	Th	$6d^2 7s^2$
	80	Hg	$5d^{10} 6s^2$	7	91	Pa	$5f^2 7d^1 7s^2$
6	81	Tl	$5d^{10} 6s^2 6p^1$		92	U	$5f^3 6d^1 7s^2$
	82	Pb	$5d^{10} 6s^2 6p^2$		93	Np	$5f^4 6d^1 7s^2$
	83	Bi	$5d^{10} 6s^2 6p^3$		94	Pu	$5f^6 7s^2$
	84	Po	$5d^{10} 6s^2 6p^4$				
	85	At	$5d^{10} 6s^2 6p^5$				
	86	Rn	$5d^{10} 6s^2 6p^6$				

hydrogen atom can be modelled as follows

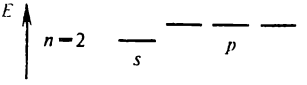


According to Pauli's exclusion principle, two electrons with opposite spins can be present in one orbital. The electron formula of helium, the next element after hydrogen, will consequently be $1s^2$. Its model will be similar to that of hydrogen, since the two *s* electrons form a single two-electron cloud:

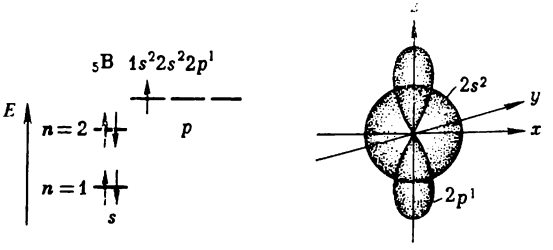


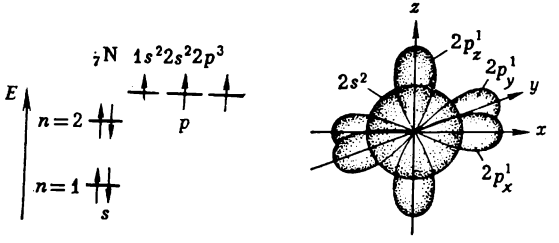
The second and the third periods contain eight elements each. In the elements of the second period, the *L* shell ($n = 2$) is filled, beginning with the orbital of the *s* subshell, and then three orbitals

of the p subshell:

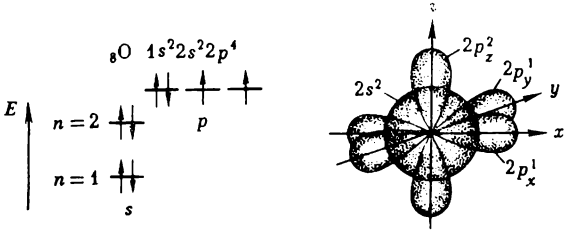


The electron formulas and models of certain elements of the second period are given below

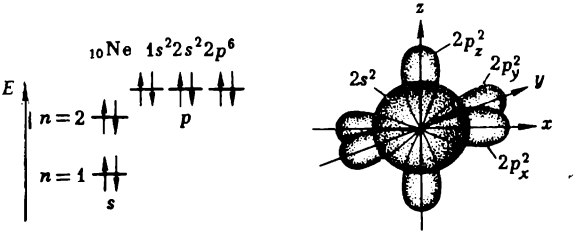




Beginning with oxygen, the $2p$ orbitals are filled by a second electron

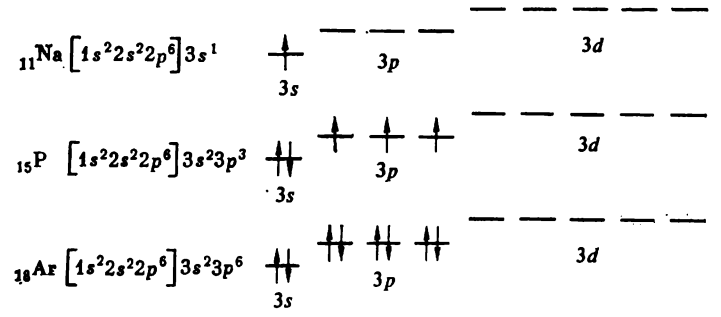


In neon, the eight outer electrons form a highly symmetrical structure consisting of four two-electron clouds:



The neon atom has the maximum possible number of electrons in the second quantum layer (shell); the total number of the elements in the second period thus corresponds to the number of electrons at the second energy level.

In the elements of the third period shell M ($n = 3$), consisting of $3s$, $3p$ and $3d$ subshells, is filled. As in the second period, the s subshell is filled in the first two elements (Na and Mg), and the p subshell in the other six (Al—Ar), as follows:



The neon structure is repeated in the first two shells (K and L) in the atoms of Na, P, and Ar; therefore the filling of the outer layer M only is shown in the diagrams.

In the last element of the third period, argon Ar (as in Ne), the s and p subshells are complete, i.e. the outer shell is a combination of four two-electron clouds (one spherical and three dumb-bells). The K, L and M shells can differ in the maxima of their distribution of electron density (Fig. 10).

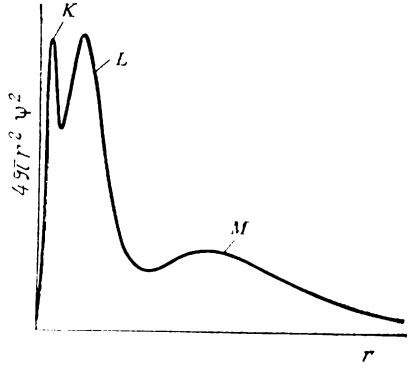


Fig. 10. Distribution of electron density in the argon atom

In contrast to the second period, the outer shell is not completely filled in elements of the third period, and the orbitals of the $3d$ subshell remain unoccupied.

Elements in which the s subshell is filled are called s elements, and those in which the p subshell is filled are known as *p elements*.

Long-period elements. The fourth and fifth periods contain 18 elements each. In elements of the fourth period, the N shell ($n = 4$), i.e. $4s$ subshells, begins to be filled. The appearance of electrons in the $4s$ state, while the $3d$ subshell is unfilled, is explained by *screening* of the nucleus by the dense, symmetrical $3s^23p^6$ electron shell. The 19th electron of

potassium (K) and the 20th electron of calcium (Ca) are repelled by this shell and occupy the more convenient as regards energy $4s$ state:

$$_{19}\mathrm{K}\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$
$$_{20}\mathrm{Ca}\ 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

As the effective charge of the nucleus increases in the scandium atom (Sc), which comes after Ca, the $3d$ state becomes more suitable as regards energy than the $4p$ subshell.

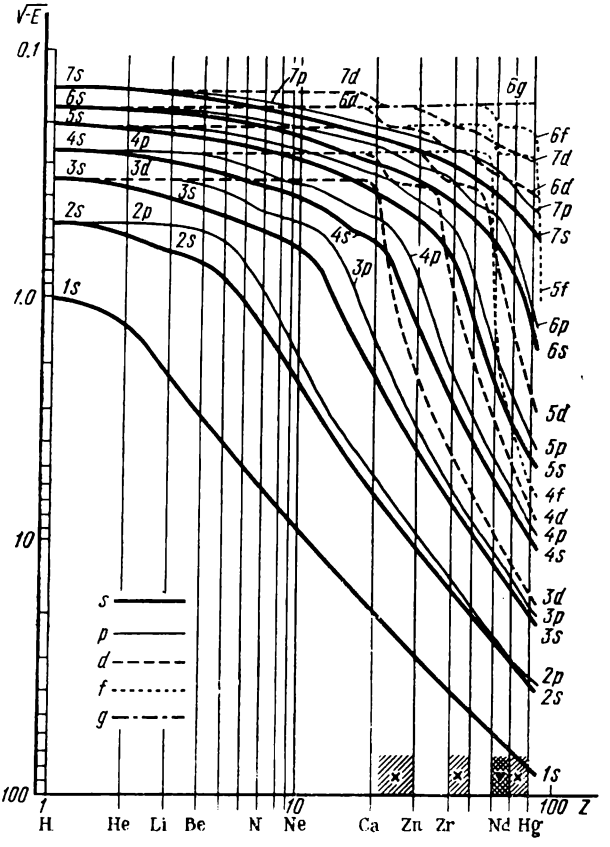


Fig. 11. Variation of the energy levels of an element with atomic number

The character of the filling of the orbitals of the atoms of K, Ca, and Sc indicates that the electron's energy does not just depend on the charge of the nucleus but also on the interaction between electrons. Figure 11 shows the dependence of the energies of atomic orbitals on an element's atomic number (on a logarithmic scale). The unit energy of an electron is 13.6 eV (the energy of the electron of an unexcited hydrogen atom). Analysis of Fig. 11 indicates that the energy of electrons of a given state ($1s$, $2s$, $2p$, etc.) decreases with increasing

atomic number Z of the element. But the character of this decrease is different for electrons of various energy states, and the curves thus intersect. For example, at $Z = 19$ and $Z = 20$, the energy curves of the $4s$ electron are therefore *below* that of the $3d$ electron, and at $Z = 21$ the curve of the $3d$ electron is below that of the $4p$ electron. Thus, the $4s$ orbital is filled in calcium and potassium and $3d$ orbital in scandium.

Since ten electrons can be present in the d state, the $3d$ orbitals are filled in the atoms of the following elements:

$$
\begin{array}{ll}
{}_{21}\mathrm{Sc} & 1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2 \\
{}_{22}\mathrm{Ti} & \ldots\ldots\ 3d^2 4s^2 \\
\ldots\ldots\ldots & \ldots \\
{}_{25}\mathrm{Mn} & \ldots\ldots\ 3d^5 4s^2 \\
{}_{26}\mathrm{Fe} & \ldots\ldots\ 3d^6 4s^2 \\
\ldots\ldots\ldots & \ldots \\
{}_{30}\mathrm{Zn} & \ldots\ldots\ 3d^{10} 4s^2
\end{array}
$$

Elements whose d orbitals are filled are called *d elements*. In d elements of the fourth period, consequently, the M shell is filled until it contains 18 electrons.

After the $3d$ orbitals have been filled (Fig. 9), the p orbitals of the outer shell begin to be filled in the next six elements (Ga—Kr). Thus the fourth period also begins with two s elements and ends with six p elements but, in contrast to the second and the third periods, there are ten d elements between the s and p elements.

In the fifth period the electron shells and subshells are filled as in the fourth period, namely, the outer shell is filled in the first two elements (s elements Rb and Sr) and in the last six (p elements In—Xe); between the s and p elements there are ten d elements (Y—Cd) in which the d orbitals of the penultimate shell (the $4d$ subshell) are filled.

The sixth period contains 32 elements and also begins with two s elements (Cs and Ba). Then follows lanthanum (La) in which the d orbitals of the penultimate shell begin to be filled:

$${}_{57}\mathrm{La}\ 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 5d^1 6s^2$$

In the fourteen elements that follow lanthanum (Ce—Lu), $4f$ orbitals of the penultimate electron shell are filled, since this state is more advantageous as regards energy than the $5d$ state (Fig. 11). The $4f$ orbitals (third outer shell) are therefore filled in these elements. Then, the $5d$ orbitals are filled (Hf—Hg); finally the period ends with six p elements (Tl—Rn). Thus, the sixth period in addition to two s elements, ten d elements, and six p elements, also contains f elements.

The seventh period has two s elements (Fr and Ra), followed by a d element Ac, and fourteen f elements (Th—Lr), and again ends with d elements (Ku, Ns, the elements with $Z = 106$, 107). The seventh period is not completed.

From what has been said it follows that there is a regular periodic repetition of similar electron structures as the charge on the nucleus increases, and consequently a recurrence of the properties of elements depends on the structure of their atom's electron shell.

At the present time the periodic law is formulated as follows: *the properties of simple substances and the properties and forms of compounds depend periodically on the charge on the nucleus of the elements' atoms.*

2.2. Structure of the Periodic System

There are many variants (over 400) of depicting Mendeleev's periodic system. The most common ones employ boxes, especially those employing eight, eighteen, and thirty-two boxes (corresponding to the capacity of shells of 8, 18, and 32 electrons). A version of a 32-box table (the longer version of the table) is given on the front inside cover and an 8-box table on the back inside cover. Table 4 is an 18-box version of the system.

Table 4. **Mendeleev's Periodic System (shortened version)**

IA	IIA										IIIA	IVA	VA	VIA	VIIA	VIIIA	Periods
															1 H	2 He	1
3 Li	4 Be										5 B	6 C	7 N	8 O	9 F	10 Ne	2
11 Na	12 Mg	IIIB	IVB	VB	VIB	VIIB	VIIIB		IB	IIB	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	3
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	4
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	5
55 Cs	56 Ba	57 La*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	6
87 Fr	88 Ra	89 Ac†	104 (Ku)	105 (Ns)	106	107												7
s		*d*									*p*							

*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
†	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 (No)	103 (Lr)
							f							

As regards the structure of their unexcited atoms, the chemical elements are divided into natural combinations which is expressed in the periodic system by arrangement of the elements in horizontal and vertical order (periods and groups).

Periods and families. A period is a series of elements whose atoms have the same number of electron shells. The number of a period coincides with the principal quantum number n of the outer shell. The difference in order of filling of the shells (whether the outer one or those closer to the nucleus) explains why the periods are of different lengths.

As we have seen, the outer shell is filled in s and p elements, the penultimate in d elements, and the third shell (from the outside) in f elements. The difference in properties is therefore more pronounced in neighbouring s (p) elements. The differences are less marked in the d and especially in the f elements, of one period.

The d and f elements in a period are grouped in *families*. In the fourth, fifth and sixth periods, the d elements fall into ten-element families, viz., the families of $3d$ (Sc—Zn), $4d$ (Y—Cd) and $5d$ (La, Hf—Hg) elements. In the sixth and seventh periods, the f elements combine in 14-element families, viz., the families of $4f$ elements, (Ce—Lu), called *lanthanides*, and the family of $5f$ elements (Th—Lr), called *actinides*.

The lanthanides and actinides are often placed outside the table (as in Table 4).

Groups and subgroups. In accordance with the maximum number of electrons in the outer shells of unexcited atoms, all elements of the periodic system are divided into *eight groups*. The position of s and p elements in the groups is determined by the total number of electrons in the outer shell. For example, phosphorus ($3s^23p^3$), with five electrons in the outer shell, belongs to group V, argon ($3s^23p^6$) to group VIII, calcium ($4s^2$) to group II, and so on.

The position of d elements in the groups is determined by the total number of s electrons in the atom's outer shell and of d electrons in the penultimate shell. In accordance with this criterion the first six elements in each family of d elements are distributed in the appropriate groups as follows: scandium ($3d^14s^2$) in group III, manganese ($3d^54s^2$) in group VII, iron ($3d^64s^2$) in group VIII, and so on. Zinc ($3d^{10}4s^2$), in which the penultimate shell is complete and the outer one contains $4s^2$ electrons, belongs to group II.

Because copper ($3d^{10}4s^1$), silver ($4d^{10}5s^1$) and gold ($5d^{10}6s^1$) have in their outer shell only one electron (due to the transfer of a $4s$ electron to the $3d$ subshell) they belong to group I. Cobalt ($3d^74s^2$) and nickel ($3d^84s^2$), rhodium ($4d^85s^1$) and palladium ($4d^{10}$), iridium ($5d^76s^2$), and platinum ($5d^96s^1$) are usually placed with Fe, Ru and Os in group VIII.

The $4f$ and $5f$ elements (lanthanides and actinides) are placed in group III in accordance with their electron structure.

The elements of groups are divided into *subgroups*. The s and p elements constitute what are called the *main* subgroups (subgroup A), and the d elements a *secondary* subgroup (subgroup B). In addition, the elements of short periods are often divided into a special subgroup of 'typical elements'. In this case, according to Nekrasov [8, pp. 167-169], the elements of a group are subdivided into three subgroups: one of typical elements, and two consisting of the elements of long periods. For example, group IV consists of the following three subgroups:

Typical elements

C $1s^2 2s^2 2p^2$

Si $1s^2 2s^2 2p^6 3s^2 3p^2$

Germanium subgroup		*Titanium subgroup*	
Ge	$[Ne]3s^2 3p^6 3d^{10} 4s^2 4p^2$	Ti	$[Ne]3s^2 3p^6 3d^2 4s^2$
Sn	$[Ar]4s^2 4p^6 4d^{10} 5s^2 5p^2$	Zr	$[Ar]4s^2 4p^6 4d^2 5s^2$
Pb	$[Kr]5s^2 5p^6 5d^{10} 6s^2 6p^2$	Hf	$[Kr]5s^2 5p^6 5d^2 6s^2$

The lanthanides and actinides are often put into other secondary subgroups, each containing two elements, one lanthanide and one actinide.

CHAPTER 3

The Periodicity of the Properties of Elements

3.1. Energy of Ionisation. Electron Affinity. Electronegativity

All the properties of elements that are determined by their atom's electron shell change regularly by period and group of the periodic system, but since the electronic structures in a series of analogous elements are *similar* but *not identical*, we observe not a simple repetition of properties in passing from one element to another in groups and subgroups, but a more or less marked *regular variation*.

The chemical nature of an element depends on the capacity of its atoms to donate or accept electrons. This can be measured quantitatively by the atom's *ionisation energy* and *electron affinity*.

Ionisation energy. By ionisation energy (or potential) I is understood the amount of energy required to remove an electron from an atom in the ground state

$$E^0 + I = E^+ + e^-$$

Ionisation energy is expressed in kJ/mole or eV/atom. Values expressed in eV/atom are numerically equal to the ionisation potential measured in volts.

A multi-electron has several ionisation energies, I_1, I_2, I_3, etc., corresponding to removal of the first, second, third electron, and so on, I_1 is thus always less than I_2, I_2 less than I_3, etc., since the charge on the positive ion formed rises as the number of electrons removed increases.

Table 5. **Ionisation Energies of the Atoms of Selected Elements (eV)**

Z	Element	I_1	I_2	I_3	I_4	I_5
1	H	13.599	—	—	—	—
2	He	24.588	54.418	—	—	—
3	Li	5.392	75.641	122.42	—	—
4	Be	9.323	18.211	153.85	217.657	—
5	B	8.298	25.156	37.92	259.298	340.217
6	C	11.260	24.383	47.87	64.48	392.00
7	N	14.534	29.602	47.43	77.450	97.863
8	O	13.618	35.118	54.89	77.394	113.873
9	F	17.423	34.987	62.65	87.23	114.214
10	Ne	21.565	41.08	63.5	97.16	126.4
11	Na	5.139	47.304	71.65	98.88	138.60
12	Mg	7.646	15.035	80.12	109.29	141.23
13	Al	5.986	18.828	28.44	119.96	153.77
14	Si	8.152	16.342	33.46	45.13	166.73
15	P	10.487	19.73	30.16	51.354	65.007
16	S	10.360	23.35	35.0	47.29	72.5
17	Cl	12.968	23.80	39.9	53.5	57.80
18	Ar	15.760	27.63	40.90	59.79	75.0
19	K	4.341	31.820	46.0	60.90	—
20	Ca	6.113	11.871	51.21	67	84.39
21	Sc	6.562	12.80	24.75	74.5	93.9
22	Ti	6.82	13.58	27.5	45.40	101.7
23	V	6.740	14.21	29.3	48.35	68.7
24	Cr	6.765	16.50	31.0	50.9	72.4
25	Mn	7.435	15.640	33.69	53.4	75.8
26	Fe	7.893	16.183	30.64	55.9	79.0
27	Co	7.87	17.06	33.49	53.2	82.2
28	Ni	7.635	18.15	35.16	56.0	79.1
29	Cu	7.726	20.292	36.83	58.9	82.7
30	Zn	9.394	17.964	39.70	61.6	86.3
31	Ga	6.09	20.514	30.70	64.3	89.8

Table 5 gives ionisation energies of selected atoms. It follows from it that an atom's ionisation energy strongly depends on its electron configuration. Completed shells are characterised, in particular, by high stability. The lowest ionisation energy I_1 is characteristic of *s* elements of the first group (Li, Na, K). Their ionisation energies I_2 increase steeply, which corresponds to the removal of an electron from the completed shell (ns^2np^6 and $2s^2$ in Li). Similarly, the removal of an electron from the completed shell (ns^2np^6 and $2s^2$ in Be) corresponds to a steep increase in the ionisation energy I_3 in *s* elements of group II (Be, Mg, Ca).

Regularity of changes in ionisation energy. The curve of the dependence of the energy of the removal of the first electron on the

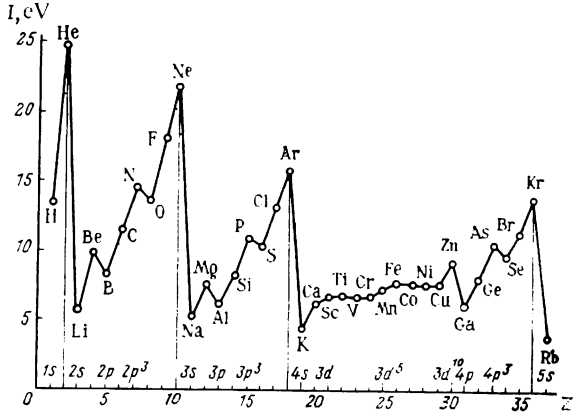


Fig. 12. Dependence of the ionisation energy of atoms on atomic number

element's atomic number (see Fig. 12) has a clearly marked periodic character. The *s* elements of group I have the lowest ionisation energies (3-5 eV) and the *s* and *p* elements of group VIII the highest. The rise in ionisation energy as we pass from the *s* elements of group I to the *p* elements of group VIII is due to the increasing effective charge on the nucleus.

In addition to the marked maxima and minima on the rising limbs of the curve there are small ones, which can be explained by two interrelated concepts, viz., those of screening of the charge of the nucleus and of electron capture.

The *screening* effect is due to the presence in the atom of other electrons between a given electron and the nucleus, which screen and weaken the effect on it of the positive charge of the nucleus and so weaken its bond with the nucleus. The screening effect understandably increases with an increase in the number of inner electron shells.

Electron *capture* is due, according to quantum mechanics, to all electrons (even outer ones) being, for a certain time, in the vicinity of the nucleus. We can therefore say that outer electrons penetrate to the nucleus through the inner electron shells. This is shown, for example, by Fig. 13 from which it is clear that the outer $3s$ electron of a sodium atom has a very high probability of being near the nucleus in the region of the inner K and L electron shells.

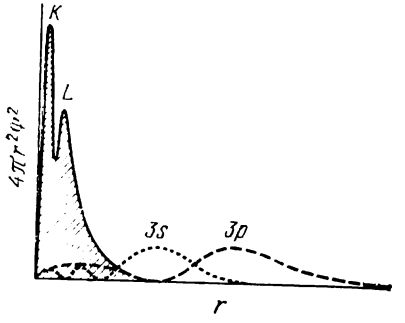


Fig. 13. Radial distribution of electron density in the sodium atom

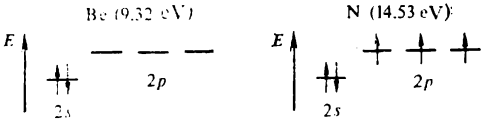
The concentration of electron density at the nucleus (degree of penetration of electrons) with the same quantum number is highest for s electrons, lower for p electrons, lower still for d electrons, and so on. With $n = 3$, for example, the penetration effect weakens in the series $3s > 3p > 3d$. What has been said is graphically illustrated by Fig. 8.

The penetration effect, of course, increases the strength of bond between the outer electrons and the nucleus. This explains, in particular, the order of filling of the s, p, d, f, . . . orbitals in multielectron atoms at a given value of n.

It can also be concluded that, because of their deeper penetration, s electrons mask the nucleus more than p electrons and the latter more than d electrons, and so on.

The mutual repulsion of electrons in one and the same shell, and especially in one and the same orbital, affects the strength of bond between them and the nucleus.

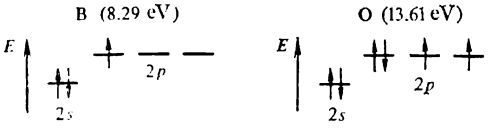
Let us consider Fig. 12 to explain this. It will be seen that the inner maxima on the curve of the first ionisation energy correspond to elements in which the outer subshells are either completely filled, i.e. s^2 (Be, Mg, Zn) or partly so, i.e. p^3 (N, P, As)



which indicates the increased stability of these configurations.

The minimum that immediately follows corresponds to the appearance of an electron in a new p subshell farther away from the nucleus (B, Al, Ga) and screened from it by the s^2 configuration, or else to the mutual repulsion of two electrons in one and the same orbital p

(O, S, Se):



In accordance with the peculiarities of their electron structures, the ionisation energies of elements of the $d(f)$ family are similar. In the Sc—Zn section of the curve (Fig. 12), there are two level portions corresponding to the filling up of the first and second halves of the $3d$ subshell. The filling of the $3d$ orbitals with one electron is completed in Mn($3d^5 4s^2$), which is marked by a certain rise in the relative stability of the $4s^2$ configuration penetrating the screen of the $3d^5$ configuration. The highest ionisation energy has Zn($3d^{10} 4s^2$) in accordance with the complete filling of the $3d$ subshell and the stabilisation of the electron pair penetrating the screen of the $3d^{10}$ configuration. The values of the third ionisation energies (see Table 5) also indicate that the d^5 and d^{10} configurations in Mn and Zn are the most stable ones.

As the atomic number of the element increases, the ionisation energy decreases in the subgroups of s and p elements, but increases in d element subgroups in the transition from $3d$ to $5d$ elements. See, for example, elements of group V:

p Elements			*d Elements*		
	Z	I_1, eV		Z	I_1, eV
As	33	9.82	V	23	6.74
Sb	51	8.64	Nb	41	6.88
Bi	83	7.29	Ta	73	7.89

The decreasing ionisation energy in the s and p element subgroups is due to the increasing screening (with increasing number of the electron shells) of the charge of the nucleus by the electrons in the inner shells.

The increasing ionisation energy in d element subgroups is due to the penetration of electrons toward the nucleus. While, for instance, the $4s$ electrons of d elements of the fourth period penetrate the shield of $3d$ electrons, the $6s$ electrons in d elements of the sixth period have to penetrate a double shield of $5d$ and $4f$ electrons.

Hence, the strength of bond of the outer s electrons with the nucleus is greater with d elements of the sixth period, and their ionization energy is greater than that of d elements of the fourth period.

Electron affinity. Electron affinity is the quantity of energy F liberated when an electron is accepted by a neutral atom E, converting it into a negative ion E^-:

$$E + e^- = E^- + F$$

It can be expressed either in kJ/mole or eV/atom. Numerically, it is equal to the ionisation energy (but with opposite sign) of a negatively charged ion E^-.

Reliable values of electron affinity have been found for only a small number of elements. It is understandable that electron affinity depends on an atom's electron configuration and that a clearly expressed periodicity is observable in its character with a rise in

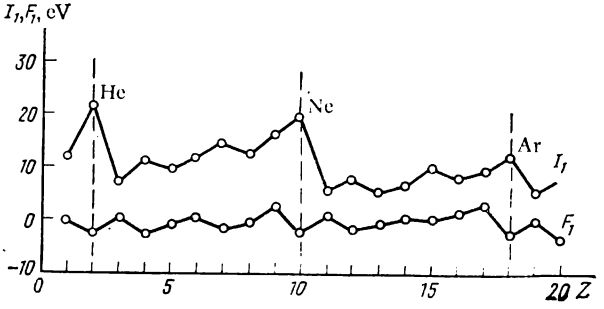


Fig. 14. Periodic dependence of atom's electron affinity and first ionisation energy on atomic number (electron affinity is taken with a reverse sign i.e. the first ionisation energies of negatively charged ions are given)

atomic number (Fig. 14). Comparison with the variation of ionisation energy indicates that the maxima and minima on the electron affinity curve are shifted one element to the left (compared with the ionisation energy curve).

It follows from the data in Table 6 and Fig. 14 that *p* elements of group VII have the highest electron affinity. Atoms with s^2 (Be, Mg, Zn) and s^2p^6 (Ne, Ar, Kr) configurations or with half-filled *p* subshell (N, P, As) have the lowest (and even negative) electron affinities. This is further proof of the high stability of these electron configurations.

Table 6. **Electron Affinity (*F*) of Selected Atoms** *

Element	*F*, eV	Element	*F*, eV	Element	*F*, eV
H	0.754	N	—0.21	Al	0.52
He	—0.22	O	1.467	Cl	3.61
Li	0.59	F	3.45	K	0.52
Be	—0.19	Ne	—0.22	Br	3.54
B	0.30	Na	0.34	I	3.29
C	1.27	Mg	—0.22		

* Electron affinities are expressed through the ionisation energies of negative ions E^-.

The attachment of an electron to the atoms of oxygen, sulphur, carbon, and certain other elements is accompanied with the liberation of energy. The attraction of an additional electron to the nucleus is thus stronger, for these elements, than the repulsion between the additional electron and the atom's electron shell.

According to quantum-mechanical calculations the attachment of further electrons, i.e. of two, three, and more, to an atom is impossible. Monatomic (simple), multiple-charged anions (O^{2-}, S^{2-}, N^{3-}) therefore cannot exist in the free state.

Electronegativity. The concept of electronegativity helps assess the ability of an atom of a given element to attract electron density (compared with the other elements in a given compound). This power obviously depends on the atom's ionisation and electron affinity. According to Mulliken, the electronegativity of an atom χ can be expressed as the half-sum of its ionisation energy and electron affinity:

$$\chi = {}^1/_2 (I + F)$$

There are around 20 different scales of electronegativity, whose values are calculated from various properties of substances. The

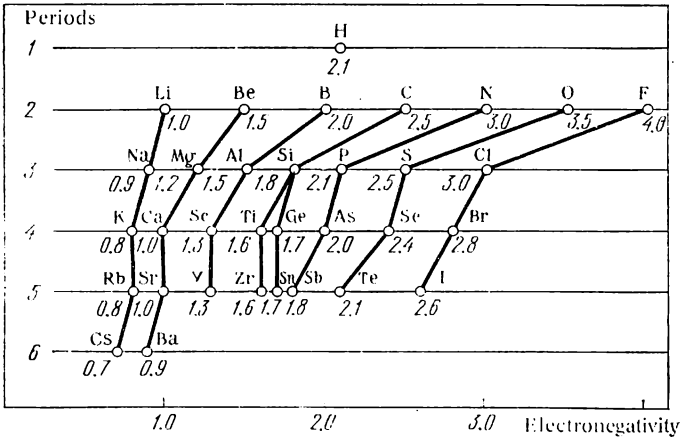


Fig. 15. Electronegativity (after Pauling)

values of the various scales differ, but the relative position of the elements in the series is roughly the same. Pauling's scale is shown in Fig. 15, which takes the electronegativity of fluorine as 4.0.

As will be seen from the figure, there is a general tendency for the value of electronegativity to increase within periods, and to decrease in subgroups. The *s* elements of group I have the lowest values and the *p* elements of group VII the highest.

Strictly speaking, one cannot assign a constant electronegativity to an element: it depends on many factors, in particular on the valent state of the element, the type of compound in which it occurs, and so on. Nevertheless, the concept is useful for a qualitative explanation of the properties of the chemical bond and compounds.

3.2. Radii of Atoms and Ions

Because of the wave character of the motion of an electron, an atom does not have strictly defined boundaries. It is therefore impossible to determine its absolute dimensions. The radius of a free atom is taken as theoretically calculated position of the main maximum of density of the outer electron clouds (Fig. 16). This is called the *orbital radius*. In practice we have to deal with the radii of atoms linked together by a chemical bond of some sort. These radii must be regarded as certain *effective* values (i.e. values displaying themselves in action). Effective radii are determined by studying the structure of molecules and crystals.

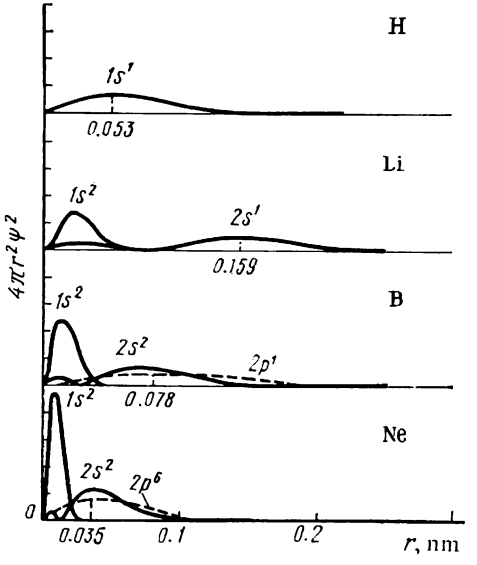


Fig. 16. Curves of the radial electron density and orbital radii of H, Li, B, and Ne atoms

The atomic and ionic radii of elements vary periodically throughout the periodic system (Fig. 17). *Within a period*, they diminish as the charge on the nucleus increases. The biggest reduction is noted in the elements of short periods, since their outer shells are filled. In long periods we observe a smoother reduction of radii within families of *d* and *f* elements, which is known as *d* or *f contraction* as the case may be.

In *subgroups* the radii of atoms and their corresponding ions in general increase, but the increase that is observed along with the same increase in charge of the nucleus in subgroups of *s* and *p* elements is more pronounced than in subgroups of *d* elements, e.g.

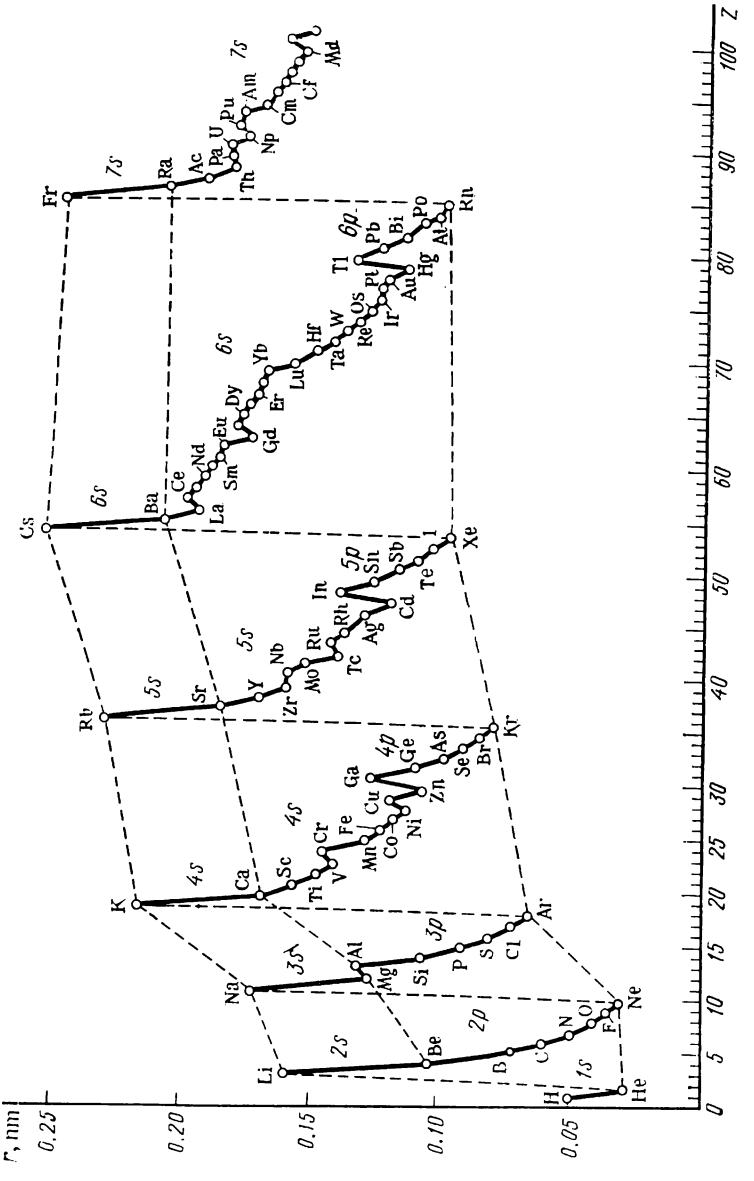


Fig. 17. Dependence of the orbital radii of atoms on atomic number

in group V*:

p Elements			*d* Elements		
	Z	*r*, nm		*Z*	*r*, nm
As	33	0.148	V	23	0.134
Sb	51	0.161	Nb	41	0.145
Bi	83	0.182	Ta	73	0.146

As will be seen, the atomic radius increases in the arsenic subgroup by 0.034 nm in the transition from As to Bi, while it increases by only 0.012 nm in the vanadium subgroup in the transition from V to Ta.

It is essential to emphasise another point about subgroups of *d* elements. The radii of their atoms and ions increase according to the transition from the fourth to the fifth period. The appropriate radii of the fifth and sixth periods of a given subgroup are approximately equal. This is due to the increase in radii arising from the increase in the number of electron shells in the transition from the fifth to the sixth period being compensated by the *f*-contraction** due to the filling of the $4f$ subshell of *d* elements of the sixth period. Because of the similar structure of their outer shells and the approximately equal radii of their atoms and ions, the properties of these *d* elements are particularly close to one another.

3.3. Secondary Periodicity

The change of properties (ionisation energies, atomic radii, etc.), in the subgroups of element is usually more or less *non-uniform*. As will be seen from Fig. 18 there are inner maxima and minima on the curves of the change in the sum of the first four ionisation energies and the orbital atomic radii in the series C—Si—Ge—Sn—Pb. Similarly, the change of other properties (see Fig. 131) is also, consequently, non-monotonous. The non-monotonous variation of the properties of elements in subgroups is known as *secondary periodicity*. It was discovered by E. I. Biron and explained by S. A. Shchukarev. The phenomenon is due to the penetration of outer electrons toward the nucleus. The non-monotonous character of the changes of atomic radii in the transition from Si to Ge and from Sn to Pb, for instance, is due to *s* electrons penetrating the shield of $3d^{10}$ electrons in Ge and the double shield of $4f^{14}$ and $5d^{10}$ electrons in Pb.

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* Effective radii, found experimentally for the metallic state of simple substances, are used.

** In this case the *f*-contraction is called the lanthanoid contraction.

Since penetrating capacity decreases in the series $s > p > d$, the inner periodicity in the change of properties is more pronounced

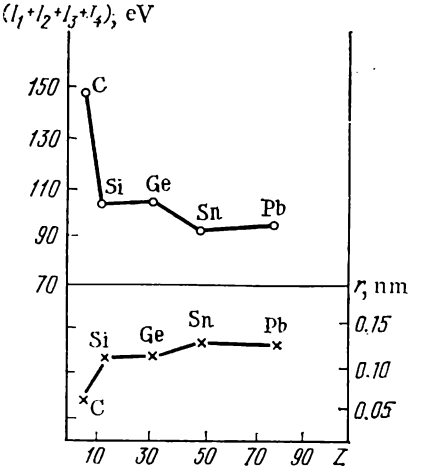


Fig. 18. Dependence of the sum of the first four ionisation energies and orbital radii of atoms of Group IV *p* elements on atomic number

in the properties of elements determined by *s* electrons. It is therefore more typical of compounds of elements of the main subgroups of the periodic system corresponding to their highest oxidation state (i.e. involvement of all the outer *s* and *p* electrons).

II

THE CHEMICAL BOND

Each day it becomes more probable that chemical affinity may be reduced to electrical processes.

V. I. Lenin, *Materialism and Empiriocriticism*

The chemical nature of a complex particle is determined by the nature, quantity, and chemical structure of its elementary components.

A. M. Butlerov

The theory of the chemical bond is the central problem of modern chemistry. Unless we know the nature of the interaction between the atoms in a substance, we cannot understand the reason for the variety of chemical compounds or picture the mechanism of their formation, or their composition, structure, and reactivity. The building of a reliable model reflecting the structure of atoms, molecules, and the nature of the forces between them, helps predict the properties of substances without resorting to experiment.

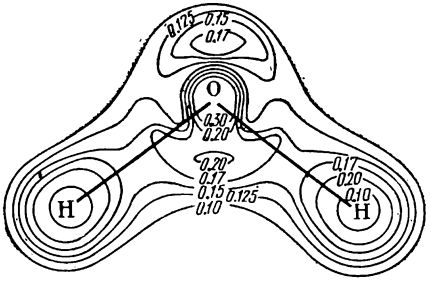


Fig. 19. Distribution of electron density in a molecule of water

A combination of chemically bound atoms (e.g. a molecule or crystal) is a complicated system of atomic nuclei and electrons. The formation of the chemical bond between them involves only the electrostatic forces of all the forces existing in nature, i.e. the forces of interaction of the electrical charges that are carried by electrons and atomic nuclei.

Modern methods of research enable us to determine the spatial arrangement of the atomic nuclei in a substance experimentally. As we have already said, one can only speak, according to quantum-mechanical concepts, about the probability of electrons' being in the field of atomic nuclei. A given spatial distribution of these nuclei corresponds to a certain distribution of electron density. To explain

the latter means in practice to describe the chemical bond in a substance, but that, of course, requires an accurate solution of Schrödinger's equation, which has been done only for the H_2^+ ion consisting of two protons and one electron. Only approximate solutions can be got for systems with two or more electrons.

The accuracy of the approximate solutions is assessed by how far they coincide with experimental data on the structure and properties of a substance. The result of one of such solutions for a molecule of water is given in Fig. 19. Object lines join the points of equal electron density.

Three main types of chemical bond are distinguished according to the character of distribution of electron density in a substance: *covalent*, *ionic*, and *metallic*. As will be seen later, these types rarely occur in 'pure' state. Various types of bond are superimposed in most cases.

CHAPTER 1

Fundamental Notions of the Chemical Bond

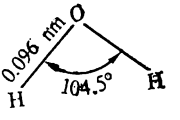
1.1. Certain Parameters of a Molecule

Information on the structure of a substance can be obtained by studying its physical and chemical properties. In particular the main parameters of a molecule, such as its internuclear distances, bond angles, and geometry, can be determined by physical research methods.

It has been established experimentally that the distance between the hydrogen and oxygen nuclei in a molecule of water is 0.096 nm. The distance between the nuclei of chemically bonded atoms is called the *bond length*.

The angle formed by imaginary lines passing through the nuclei of atoms joined by a chemical bond is called the *valence* or *bond angle*. In a water molecule it is 104.5°.

A molecule of water is thus angular (Fig. 19). To visualise it we can take it that there are two O—H chemical bonds (the d_{OH} length is 0.096 nm) at an angle of 104.5° ($\angle HOH = 104.5°$). The structure of a molecule of water can be depicted as follows:



The most important characteristic of a chemical bond is its *energy*, which determines its strength. The measure of bond strength is the

amount of energy needed to break the bond. The bond energy of a diatomic molecule is the energy of its dissociation into atoms. For example, the energy of dissociation D, and hence the bond energy E in an H_2 molecule is 435 kJ/mole. The bond energy of a fluorine molecule F_2 is 159 kJ/mole, and of a nitrogen molecule N_2 940 kJ/mole. The mean bond energy of a polyatomic molecule of the AB_n type is $1/n$ of the energy of its dissociation into atoms:

$$AB_n = A + nB, \quad E_{AB} = D/n$$

For example, the energy absorbed in the process

$$H_2O = 2H + O$$

is 928 kJ/mole H_2O. But both bonds O—H in the water molecule are equivalent and the mean bond energy is $E_{O-H} = D/2 = 928/2 = 464$ kJ/mole.

Bond lengths and energies, bond angles, and the experimentally determined magnetic, optical, electrical, and other properties of substances depend directly on the character of the distribution of electron density. A final conclusion about the structure of a substance can be drawn after comparing the information obtained by the various methods. The quantum-mechanical theory of the chemical bond sums up the experimentally obtained data on the structure of matter.

A chemical bond is mainly brought about by what are called valence electrons. In the s and p elements, the valence electrons are the electrons of the outer shell, while in the d elements, they are s electrons of the outer shell and d electrons of the penultimate shell.

1.2. The Nature of the Chemical Bond

A chemical bond is formed only when two or more atoms come into close proximity to one another and the overall energy of the system (the sum of the kinetic and potential energies) is reduced.

Let us consider the simplest of all possible molecular systems, the molecular ion of hydrogen, H_2^+, in which one electron moves in the field of two nuclei (protons). This particle is obtained when a molecule of hydrogen H_2 is radiated by electrons. The distance between the nuclei is 0.106 nm, while the bond energy, i.e. the energy of dissociation into the atom H and the ion H^+ is 255.7 kJ/mole. The particle is thus quite stable.

Let us assume that a proton H_A^+ and a hydrogen atom H_B (a proton H_B^+ plus electron e^-) have been brought close together. As they approach, electrostatic forces of two types arise between them, forces of attraction of the electron to both nuclei and forces of repulsion between the two nuclei (Fig. 20).

The force of internuclear action $f_{H_AH_B}$ is always directed along the axis uniting the nuclei centres and tends to drive them further

apart. A molecule will probably be formed in this case if the resultant of the forces of attraction and repulsion is zero. In other words, the repulsion of the nuclei (protons H_A^+ and H_B^+) must be compensated by the attraction of the electron toward the nuclei. The effectiveness

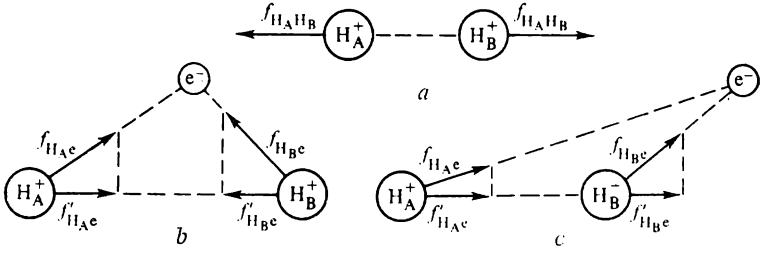


Fig. 20. The forces interacting in H_2^+

of the attraction depends on the electron's position relative to the nuclei. It is impossible, of course, to determine its position in the molecule, but it can be considered probable that it will be in the space around the nuclei. At any moment of time it may be in the position *b* shown in Fig. 20. At another moment it will be in another position, for example *c* (Fig. 20).

Let us compare the resultant of the forces of attraction and repulsion for these configurations. When an electron is in position *b*, its attraction to the protons (forces f_{H_Ae} and f_{H_Be}) encourages their convergence (forces f'_{H_Ae} and f'_{H_Be}). In configuration *c* another situation arises. The forces of attraction (f'_{H_Ae} and f'_{H_Be}) are then oriented in one direction and do not compensate the repulsion of the protons.

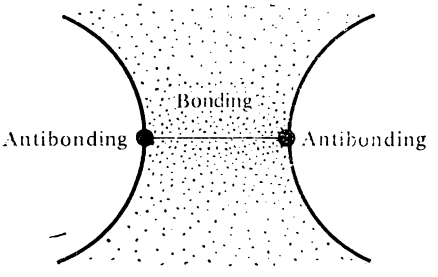


Fig. 21. Bonding and antibonding regions in a homonuclear diatomic molecule

Thus, in accordance with the electron's position relative to the two protons, there are *bonding* and *antibonding* regions (Fig. 21). When an electron is in a bonding region, a chemical bond is formed. When the electron is in an antibonding region, a chemical bond is not formed.

A chemical bond thus arises when an electron is between the nuclei. It is formed through electrostatic interaction of the positively charged nuclei and negatively charged electrons.

1.3. The Curve of Potential Energy for a Molecule

As we have already said, the energy of the electron and distribution of electron density can be calculated for a molecular ion of hydrogen H_2^+ using the Schrödinger equation. To calculate the electron density it is assumed that the nuclei are immovable. This assumption holds because of the great difference between the masses of the electrons and nuclei: if the nuclei moved, the electron density would be instantaneously adapted to their new position, whereas their position does not depend on the motion of the light electrons. Once we have calculated the energy of the system for various internuclear distances we can plot a graph showing the dependence of the system's energy on the internuclear distance. When the distance between the nuclei changes, the energy of the electron and of the molecule also change. Consequently the curves of the molecule's potential energy (see Fig. 22) reflect the dependence of the electron's energy on the internuclear distance.

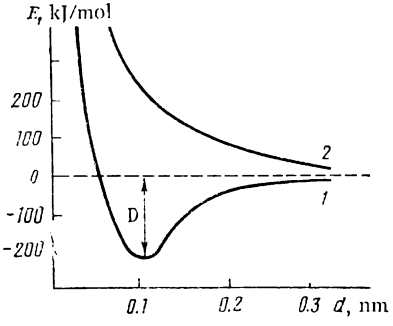


Fig. 22. The lowest energy levels of the H_2^+ ion depending on the internuclear distance

Figure 22 shows possible levels of the energy of H_2^+ depending on the internuclear distance, which is plotted on the x-axis and the potential energy of the system along the y-axis. It will be easily guessed that the ground state of the molecular ion H_2^+ corresponds to the lowest energy level. The character of the lower curve in Fig. 22 can be explained by that the forces of attraction first prevail, then the repulsive forces becoming effective as the proton and the hydrogen atom begin to converge so that there is a steady reduction of the system's potential energy and, as the minimum is reached, a steep rise. The minimum on the potential energy curve corresponds to the most stable state of a system consisting of two protons and one electron, i.e. to the formation of a molecular ion of hydrogen H_2^+. The energy minimum on the curve corresponds to equilibrium distance between the protons ($d_{HH} = 0.106$ nm); the depth of the minimum corresponds to the energy of the dissociation of the H_2^+ ion into an H atom and an H^+ proton ($D_{H_2^+} = 255.7$ kJ/mole). The lower curve corresponds to the state when the electron is in the bonding region (see Fig. 21). The energy level (orbital) of this position is called *bonding* and is designated by σ.

The next energy level of the molecular hydrogen ion (Fig. 22, curve *2*) has no minimum and a molecule therefore cannot be formed

in it. This situation arises when the electron is behind the nuclei, i.e. in the antibonding region. The energy level or orbital here is *antibonding* and designated by σ^*.

Thus, the formation of a chemical bond in H_2^+ is explained by the motion of the electron about the two nuclei; a region of high density of the negative charge arises between the nuclei which pulls the positively charged nuclei together. The attraction lowers the potential energy of the system, and the total energy of the system consequently also decreases to give rise to a chemical bond.

We have given a simplified interpretation of the reasons for the lowering of the system's total energy. In fact the picture of the change of the electron's potential and kinetic energies during the formation of a molecule from atoms is complicated. But according to the *virial theorem*, the mean potential energy of particles $\overline{U}$ in a system in which coulomb forces operate is equal to twice their mean kinetic energy $\overline{K}$: $\overline{U} = -2\overline{K}$ (with the sign reversed), i.e. $\Delta\overline{U} = -2\Delta\overline{K}$. Since the total energy $\overline{E} = \overline{U} + \overline{K}$, its change $\Delta\overline{E} = 1/2\Delta\overline{U}$ and $\Delta\overline{E} = -\Delta\overline{K}$.

CHAPTER 2

Molecular Orbital Theory

2.1. Molecular Orbitals

Since a precise solution of the Schrödinger equation is impossible for molecules more complex than H_2^+, various approximate methods have been proposed to calculate the wave function, and consequently the distribution of electron density in a molecule. Two approaches are widely used: (a) the theory of valence bond (VB) and (b) the theory of molecular orbitals (MO). The former method was developed mainly by Heitler and London, Sleter and Pauling, and the latter by Mulliken and Hund.

In the theory of molecular orbitals a molecule is regarded as a system of nuclei and electrons in which each electron moves in the field of the other electrons and all the nuclei.

The principle of the MO method is quite simple: the quantum-mechanical regularities established for the atom are extended to a more complicated system, the molecule. Underlying the theory is a concept of the 'orbital' structure of the molecule, i.e. that all the electrons in a given molecule (as in the atom) are distributed in corresponding orbitals, each of which is characterised by a set of quantum numbers reflecting the electron's properties at a given energy level. The specific character of the molecular state is that a molecule contains several atomic nuclei, i.e. that molecular orbitals, unlike unicentric atomic orbitals, are multicentred (common

to two or more atomic nuclei). By analogy with the atomic s, p, d, f, . . . orbitals, molecular orbitals are designated by the Greek letters σ, π, δ, φ, ...

To describe a molecule in accordance with the MO theory is to determine the type of its orbitals and their energies, and to reveal the way the electrons are distributed in the orbitals in order of their increasing energy, using the Pauli exclusion principle and the Hund rule, i.e. to solve the same problems as we have discussed for the electron structure of atoms.

Since molecular orbitals are multicentred, their configuration is more complicated than that of atomic orbitals. As the simplest approximation they can be represented as the result of linear combination of orbitals of the atoms forming the molecule. In other words, their formation can be represented as the result of the summation and subtraction of the combined atomic orbitals. If, for example, the orbitals of atoms A and B forming the molecule AB are designated by ψ_A and ψ_B, their linear combination (summation and subtraction) yields molecular orbitals of two types: summation gives a molecular orbital Ψ_+ and subtraction Ψ_-

$$\Psi_+ = c_1\psi_A + c_2\psi_B$$
$$\Psi_- = c_3\psi_A - c_4\psi_B$$

The coefficients c indicate the involvement of the corresponding orbitals in the formation of molecular orbitals.

This method is known as the *linear combination of atomic orbitals*, or LCAO-MO for short (the linear combination of atomic orbitals is a molecular orbital). A combination of N atomic orbitals gives N molecular orbitals.

Let us consider the shape and relative energy of the two-centre molecular orbitals arising from linear combination of two 1*s* orbitals. For the case of diatomic molecules with similar nuclei (homonuclear molecules) the contribution of the atomic orbitals to the molecular orbital will be equal, i.e. $c_1 = c_2$ and $c_3 = c_4$.

The summation and subtraction of two atomic orbitals is shown in Fig. 23 assuming that the atomic nuclei are along the z-axis. With the given internuclear distance, the initial atomic orbitals overlap. If the overlapping parts of the orbitals have a wave function of the same sign, it corresponds to *positive overlapping*, i.e. summation of the atomic orbitals. If the overlapping parts of the orbitals have wave functions of opposite sign the overlapping is *negative*, i.e. the atomic orbitals are subtracted.

The summation of atomic orbitals yields two-centre molecular orbital $\sigma 1s$. It means that the molecular orbital is characterised by increased electron density in the space between the nuclei, so that this orbital is more advantageous as regards energy than the initial atomic orbitals. Such a molecular orbital is called *bonding* (see

Fig. 23). The plus sign on the depiction of it means that the wave function is positive throughout, i.e. has one and the same sign. The orbital has no node.

The subtraction of atomic orbitals corresponds to a change in the sign of the wave function (see Fig. 21), yielding a two-centre orbital.

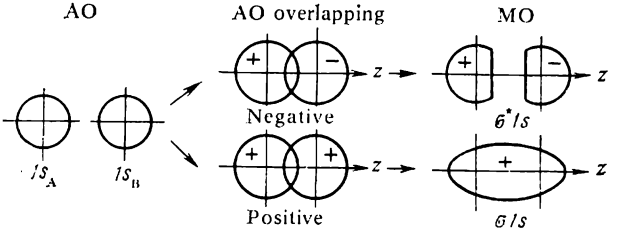


Fig. 23. Diagram of the formation of bonding and antibonding molecular δ_s orbitals

In this orbital electron density is concentrated behind the nuclei and is zero at the centre. Such an orbital is less advantageous as regards energy than the initial atomic orbitals. The orbital is called *antibonding* and is designated σ^*1s.

The character of the distribution of electron density in the initial atomic and resultant molecular orbitals is shown in Fig. 24. Since

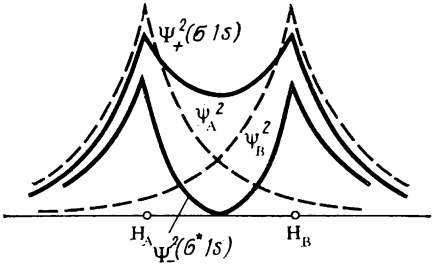


Fig. 24. Curves of the probability of finding an electron in the atomic (broken) line and molecular (solid line) orbitals of the H_2^+ molecular ion

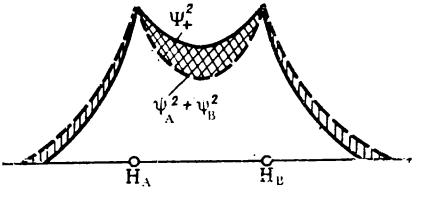


Fig. 25. Distribution of electron density in the H_2 molecule (solid line) and the sum of probabilities of finding electron in the 1*s* orbitals of two hydrogen atoms (broken line)

the orbitals (to be more exact, wave functions) are summated (subtracted), the electron density between the nuclei (characterised by the square of the wave function), it should be noted, is higher than the sum of the densities of the electron clouds of isolated atoms for the same distance. The distribution of electron density in the hydrogen molecule H_2 is shown in Fig. 25. It is much higher in the region

between the nuclei (cross-hatched) than the sum of the densities of two isolated atoms. The probability of an electron's being between the two nuclei (in the binding region) is increased by the removal of electrons from the antibonding region (light hatching).

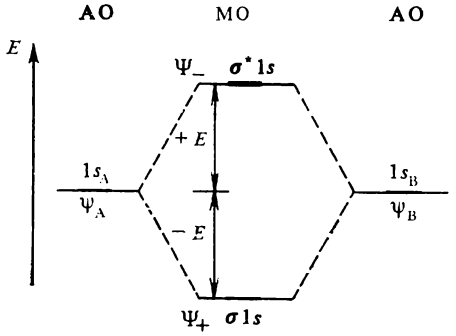


Fig. 26. Energy diagram of the levels of the atomic and molecular orbitals of hydrogen

The formation of molecular orbitals from atomic orbitals is usually depicted in the form of *energy diagrams*, in which the energy of the E orbitals is plotted against the vertical axis (Fig. 26). The distribution of electrons in molecular orbitals explains many of the properties of molecules.

2.2. Diatomic Homonuclear Molecules

Diatomic homonuclear molecules of elements of the first period. In elements of the first period the valence orbital is the $1s$ orbital. The diagram in Fig. 26 is therefore valid only for binuclear molecular formations H_2^+, H_2, He_2^+, He_2.

The H_2^+ ion consists of two protons and one electron. Its sole electron must naturally occupy the orbital that is the most advantageous as regards energy. This is the $\sigma 1s$ orbital (Fig. 26). So the electron formula of the ion in the ground state is

$$H_2^+ \ [(\sigma 1s)^1]$$

The formation of this ion from an atom of hydrogen and a proton can be represented by the following equation

$$H(1s^1) + H^+(1s^0) = H_2^+ \ [(\sigma 1s)^1]$$

The H_2 molecule has two electrons. According to the principle of least energy and the Pauli exclusion principle, these two electrons with opposite spins also fill the $\sigma 1s$ orbital. The reaction of formation of a hydrogen molecule from atoms can be represented as follows (using MO theory designations):

$$2H \ [1s^1] = H_2 \ [(\sigma 1s)^2]$$

In the molecular ion of dihelium, He_2^+, there are three electrons, two of which fill bonding and the third antibonding orbitals:

$$He_2^+ \ [(\sigma 1s)^2(\sigma^* 1s)^1]$$

In the system of two helium atoms there are four electrons, two in the bonding orbital and two in the antibonding orbital.

Bond energy, length, and order. Bond energy, length, and order can be determined from the character of distribution of electrons in molecular orbitals. The presence of an electron in the bonding orbital of course indicates a concentration of electron density between nuclei, and that causes a contraction of the internuclear distance and stabilisation of the molecule. The presence of an electron in an antibonding orbital, on the contrary, means that electron density is concentrated behind the nuclei. In that case the bonding energy is reduced, while the internuclear distance increases:

Molecular orbitals	H_2^+	H_2	He_2^+	He_2
$\sigma^* 1s$	—	—	↑	↑↓
$\sigma 1s$	↑	↑↓	↑↓	↑↓
Dissociation energy D, kJ/mole	255.7	435	230	—
Internuclear distance (bond length) d, nm	0.106	0.074	0.108	—
Bond order	0.5	1	0.5	0

In the series H_2^+—H_2—He_2^+, as the bonding orbital is filled, the energy of dissociation of the molecules increases; with the appearance of an electron in the antibonding orbital, the dissociation energy, on the contrary, decreases. The internuclear distance first decreases and then increases.

A molecule of helium does not exist in an unexcited state since the number of bonding and antibonding electrons in it is identical. One can also say that an H_2 molecule with similar (parallel) spins of the electrons cannot exist. In this case one electron is in the bonding and the other in the antibonding orbital.

The distribution of electrons along the orbitals helps assess bond order (multiplicity) as half the difference in the number of bonding and antibonding electrons:

$$\text{bond order} = \frac{\text{number of bonding electrons} - \text{number of antibonding electrons}}{2}$$

It can easily be calculated that the bond order in a molecular ion of hydrogen and in the dihelium ion is 0.5, in the hydrogen molecule 1, and in the system of two unexcited atoms of helium zero.

Diatomic homonuclear molecules of second period elements. In elements of the second period, the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals are also involved in the formation of molecular orbitals, in addition to the $1s$ orbitals. For the atomic formation of stable molecular

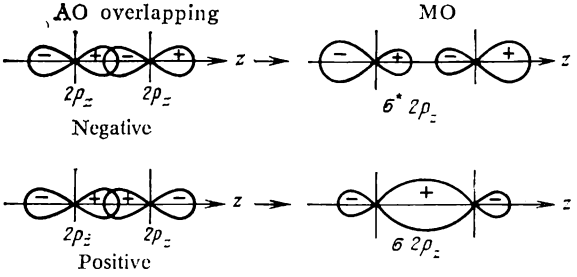


Fig. 27. Diagram of the formation of bonding and antibonding molecular σ_z orbitals

orbitals, they have to have similar energies and overlap considerably. Only those orbitals are combined, when bonding and antibonding molecular orbitals are formed, whose spatial arrangement corresponds to their positive or negative overlapping.

If the energies of $2s$ and $2p$ orbitals differ significantly, there is no overlapping of the type $s_A—p_B$ ($s_B—p_A$). Because of their small size, the inner $1s$ orbitals hardly overlap and the combination $1s_A - 1s_B$ can therefore be disregarded. Then the following combinations of the valence orbitals of elements of the second period meet the other requirements.

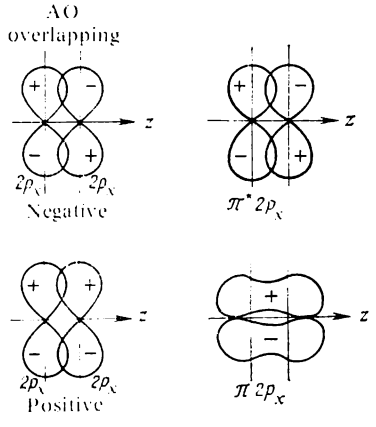


Fig. 28. Diagram of the formation of bonding and antibonding molecular π_x orbitals

A combination of $2s$ orbitals (as in the case with $1s$ orbitals) corresponds to the formation of two molecular σ orbitals: $\sigma 2s$ and $\sigma^* 2s$ orbitals.

Let us assume that the overlapping of orbitals is along the z-axis. Then with a combination of orbitals of the p type, the character of the overlapping of the $2p_z$ orbitals differs substantially from that of the $2p_x$ and $2p_y$ orbitals. The combination of $2p_z$ atomic orbitals, which are extended along the z-axis, gives molecular σ orbitals: $\sigma 2p_z$ and $\sigma^* 2p_z$ orbitals (Fig. 27) while the combination of two $2p_x$ orbitals gives the π molecular orbitals: $\pi 2p_x$ and $\pi^* 2p_x$ orbitals (Fig. 28). If two $2p_y$ orbitals are combined instead of the

$2p_x$ atomic orbitals, similar molecular orbitals of the π type (but tilted 90° about the molecule's internuclear axis) will be obtained. Since the energies of the $2p_x$ and $2p_y$ orbitals are equal and they overlap in a similar manner, the $\pi 2p_x$ and $\pi 2p_y$ molecular orbitals arising

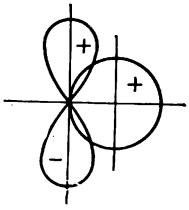


Fig. 29. Zero overlapping of orbitals

have the same energy and shape; the same holds for $\pi^* 2p_x$ and $\pi^* 2p_y$ orbitals. Thus, π molecular orbitals consist of doubly degenerate energy levels (π and π^*).

Other combinations of atomic orbitals can also be represented, for example, the overlapping shown in Fig. 29. But such overlapping

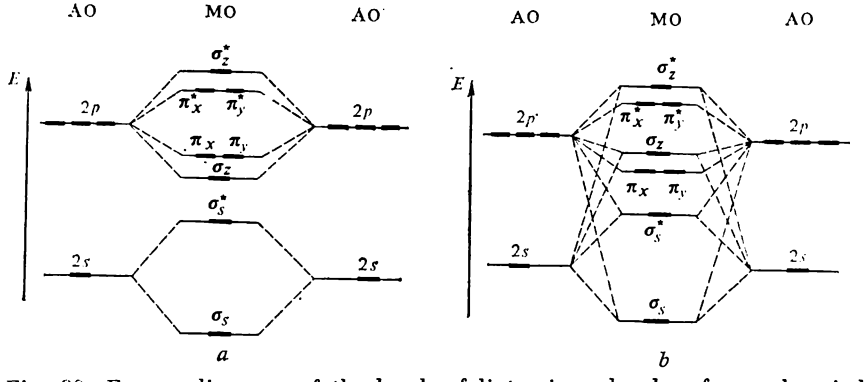


Fig. 30. Energy diagrams of the levels of diatomic molecules of second period elements with (*a*) considerable and (*b*) insignificant energy differences of the 2*s* and 2*p* orbitals

does not cause formation of a molecular orbital since the positive overlapping in this case will be completely compensated by the negative overlapping (*zero overlapping*).

Spectroscopy shows that the molecular orbitals of diatomic molecules of the elements at the end of the period can be arranged in the following series in order of increasing energy:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < \pi 2p_x = \\ = \pi 2p_y < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

Energy diagrams of the levels of atomic and molecular orbitals of diatomic molecules of second period elements are shown in Fig. 30*a*. They can be used to determine the distribution of electrons in the

orbitals of molecules; the energy order of the orbitals, the Pauli principle, and the Hund rule must be taken into account. The reaction of formation of the F_2 molecule from atoms, for example, using the MO theory system of designations, can be written as follows:

$$2F\ [1s^2 2s^2 2p^5] = F_2\ [(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2$$
$$(\sigma^* 2s)^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi^* 2p_x)^2(\pi^* 2p_y)^2]$$

As has been said above, since the overlapping of the $1s$ orbitals is insignificant, the involvement of the $1s$ electrons in the formation of bonds can be disregarded and the inner electrons can be regarded as nonbonding, i.e. belonging to separate atoms. Then the electron configuration of the fluorine molecule F_2 can be represented by the formula

$$F_2\ [KK\ (\sigma_s)^2\ (\sigma_s^*)^2\ (\sigma_z)^2\ (\pi_x)^2\ (\pi_y)^2\ (\pi_x^*)^2\ (\pi_y^*)^2]$$

where K is the electron configuration of the K shell.

When the energy of the $2s$ and $2p$ orbitals is close, the electrons in the $\sigma 2s$ and $\sigma 2p_z$ orbitals are mutually repelled so that $\pi 2p_x$ and $\pi 2p_y$ orbitals are more advantageous than the $\sigma 2p_z$ orbital. The order of filling of the molecular orbitals is slightly altered in this case (Fig. 30*b*) and is as follows:

$$\sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^* 2p_x = \pi^* 2p_y < \sigma^* 2p_z$$

The energy difference of the $2s$ and $2p$ orbitals in the period increases as we pass from group I to group VIII (see Fig. 11). The sequence of molecular orbitals given here is therefore characteristic of diatomic molecules of elements at the beginning of the period up to N_2. Thus, the electron configuration of the nitrogen molecule in the ground state has the following form:

$$N_2\ [KK\ (\sigma_s)^2\ (\sigma_s^*)^2\ (\pi_x)^2\ (\pi_y)^2\ (\sigma_z)^2]$$

Molecular orbitals are designated by the appropriate symbols on the basis of their behaviour in symmetry operations. If σ type orbitals (see Figs. 23 and 27), for example, are imagined as rotated 180° around the molecule's internuclear axis, the resultant shape of the orbitals will not differ from the original configuration. With such rotation the sign of their wave function will not change: the orbital is *symmetrical* relative to this operation. The s atomic orbital behaves similarly. Molecular orbitals symmetrical as regards rotation about the internuclear axis are designated by the Greek letter σ (analogous to the Latin s).

It will readily be seen that molecular orbitals of the π type (see Fig. 28) will be *antisymmetric* when rotated 180° about the internuclear axis, the sign of the wave function being reversed. The p atomic orbital behaves similarly. Molecular orbitals of this type are therefore designated by the Greek letter π (the analogue of the Latin p).

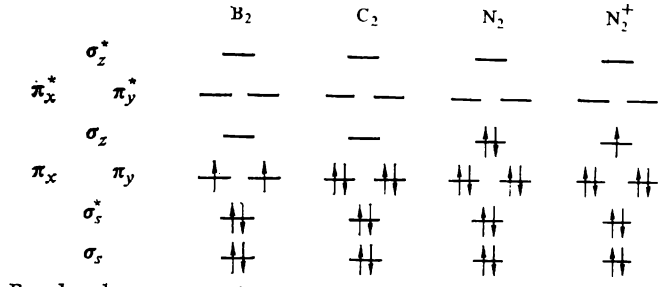
The symmetry operation known as *inversion* is used to describe orbitals. This operation consists in the following. A straight line is drawn from any point on an orbital through its centre to a symmetrically located second point. If the sign of the wave function at the new point does not change, the orbital is called symmetrical relative to inversion. To designate symmetrical and antisymmetrical behaviour relative to inversion, the German words *gerade* and *ungerade* are often used (meaning 'even' and 'odd' respectively). σ_s and σ_z molecular orbitals are even and can be designated σ_g. π_x^* and π_y^* orbitals are

also even (*gerade*) and can be designated π_g^*. σ_s^* (σ_z^*) and $\pi_{x,y}$ orbitals, on the contrary, are odd (*ungerade*) and designated σ_u^* and π_u, respectively. An asterisk designates antibonding orbitals, bonding molecular orbitals are unmarked. When we use these symbols the electron configuration of the fluorine molecule can be written as follows:

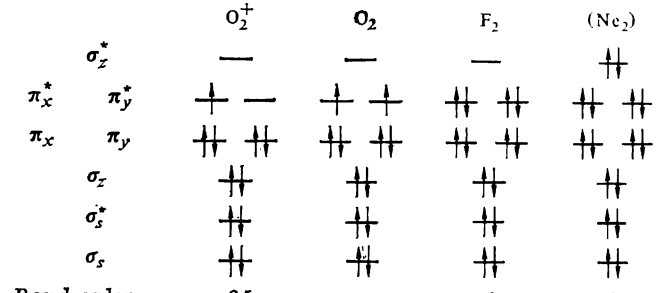
$$(1\sigma_g)^2\ (1\sigma_u^*)^2\ (2\sigma_g)^2\ (2\sigma_u^*)^2\ (3\sigma_g)^2\ (1\pi_u)^4\ (1\pi_g^*)^4$$

The numerals before the symbol designate the number of the energy level, including the orbitals of the given symmetry.

Properties of molecules of second period elements. Data characterising the bond energy, length, and order in homonuclear molecules of the elements of the second period are given below:



	B_2	C_2	N_2	N_2^+
Bond order	1	2	3	2.5
Bond length, nm	0.159	0.131	0.110	0.112
Dissociation energy, kJ/mol	288.4	627	940	828



	O_2^+	O_2	F_2	(Ne_2)
Bond order	2.5	2	1	0
Bond length, nm	0.112	0.121	0.142	—
Dissociation energy, kJ/mol	629	494	159	—

Bond length decreases and the dissociation energy of molecules increases in the series B_2—C_2—N_2 as the bonding orbitals are filled Conversely, in the series N_2—O_2—F_2, bond length increases as the

antibonding orbitals are filled, while the dissociation energy of the molecules decreases. The Ne_2 molecule is generally unstable because the number of bonding and antibonding electrons is identical. The fact that the other inert gases are also monatomic is similarly explained. The relationship between dissociation energy of molecules and number of valence electrons is shown in Fig. 31.

Loss of an electron from an antibonding orbital increases the energy of dissociation and reduces the internuclear distance. This is evident, for example, when the data for O_2 and O_2^+ are compared. Conversely, loss of an electron from the bonding orbital reduces the dissociation energy and increases the internuclear distance as will be seen by comparing the data for N_2 and N_2^+.

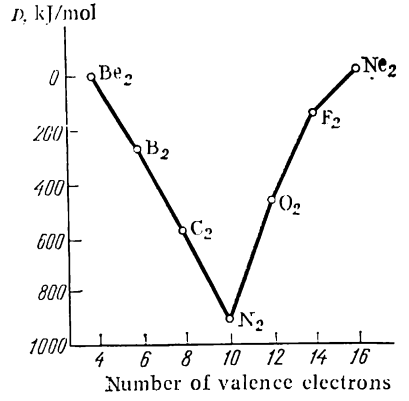


Fig. 31. Dependence of the dissociation energy of molecules on the number of valence electrons

Ionisation energy of molecules. Ionisation energy depends directly on the distribution of electrons in bonding and antibonding molecular orbitals. As we have seen, the bonding electrons are closer to the nucleus in a diatomic molecule than in the atom; the situation is the opposite with antibonding electrons. The ionisation energy of a molecule, whose outer occupied energy level is bonding, is thus higher than that of a free atom. The ionisation energy of the N_2 molecule (15.58 eV), for example, is higher than that of the nitrogen atom (14.53 eV). If the outer occupied level is antibonding, the molecular ionisation energy is lower than that of the atom. The ionisation energy of the O_2 molecule (12.08 eV), for example, is lower than that of the oxygen atom (13.62 eV).

Magnetic properties of molecules. The character of distribution of electrons in molecular orbitals can also be used to explain the magnetic properties of molecules. *Paramagnetic* and *diamagnetic* substances are distinguished according to their magnetic properties (see p. 162). *Paramagnetic* substances are those having unpaired electrons while *diamagnetic* substances have all their electrons paired.

An oxygen molecule (see p. 63) has two unpaired electrons and the molecule is paramagnetic; a fluorine molecule has no unpaired electrons and is consequently diamagnetic. The B_2 molecule (see p. 63) and H_2^+ and He_2^+ molecular ions (see p. 59) are paramagnetic while the C_2, N_2 and H_2 molecules are diamagnetic.

Colour. The theory of molecular orbitals also explains the colour of substances. Colour is the result of selective absorption of the visible part of the electromagnetic spectrum. If, for example, a substance absorbs the yellow-green region of the spectrum, i.e. wavelengths of 500-560 nm, its observed colour is violet. That, for example, is the colour of molecular iodine. The energy diagram of the iodine orbitals is similar to that of the fluorine molecule. The colour of iodine can be considered as due mainly to the transition of an electron from the excited π^* orbital to the free σ^* orbital, which happens, according to the fundamental equation of the quantum theory, $\Delta E = h\nu = hc/\lambda$, through the absorption of electromagnetic radiation with a wavelength of the order of 520 nm, i.e. of quanta corresponding to the yellow-green region of the spectrum.

2.3. Diatomic Heteronuclear Molecules

Heteronuclear diatomic molecules, like homonuclear diatomic ones, are described by the LCAO-MO method. But since the atoms are different, the energy of the atomic orbitals and their relative contribution to the molecular orbitals are also different:

$$\Psi_+ = c_1\psi_A + c_2\psi_B, \quad \Psi_- = c_3\psi_A - c_4\psi_B$$

The orbital of the more electronegative atom makes a bigger contribution to the bonding orbital and the atomic orbital of the less

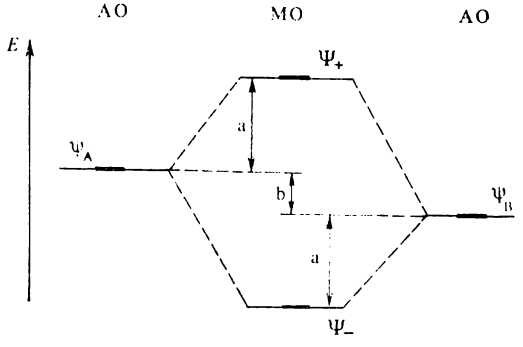


Fig. 32. Energy diagram of the molecular orbitals of a heteronuclear molecule

electronegative atom to the antibonding orbital. Let us assume that atom B is more electronegative than atom A. Then $c_2 > c_1$; $c_3 > c_4$.

Bonding orbitals are closer in energy to the orbitals of the more electronegative atom and antibonding orbitals to the orbitals of the less electronegative atom (Fig. 32). Figuratively speaking, the electron in the bonding orbital spends the greater part of the time

around the nucleus of the more electronegative atom, and that in the antibonding orbital around the nucleus of a less electronegative atom.

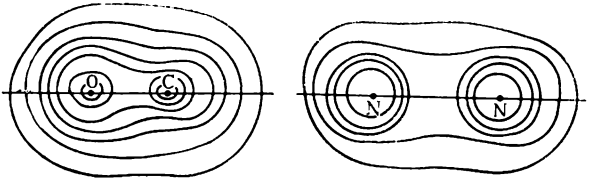


Fig. 33. Contour diagram of the distribution of electron density in (*a*) CO and (*b*) N_2 molecules

The difference in the energy of the initial atomic orbitals determines the polarity of the bond. Value *b* (Fig. 32) is the measure of ionicity of the bond and value *a* of its covalency.

The character of the distribution of electron density in the heteronuclear CO molecule and of the homonuclear molecule N_2 isoelectronic to it is shown in Fig. 33.

2.4. Triatomic Linear Molecules

The BeH_2 molecule. In accordance with the LCAO method, the molecular orbital in polyatomic molecules consists of the orbital of the central atom ($\psi_{c.a}$) and the group orbital (ψ_{gr})

$$\Psi_+ = c_1\psi_{c.a.} + c_2\psi_{gr}; \quad \Psi_- = c_3\psi_{c.a.} - c_4\psi_{gr}$$

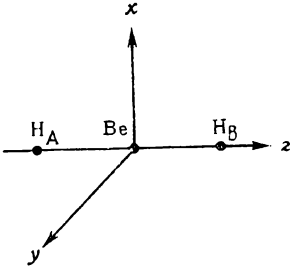


Fig. 34. Diagram of the coordinates of a BeH_2 molecule

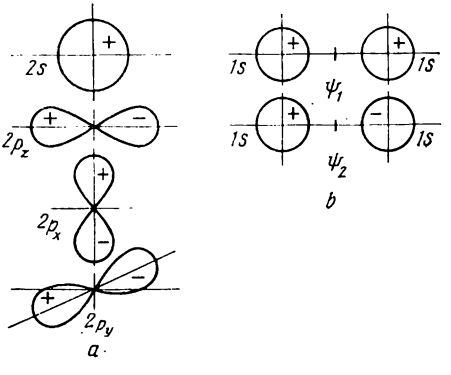


Fig. 35. Orbitals of (*a*) the central atom and (*b*) the group orbitals of ligands in a three-centre linear molecule

The latter is the result of linear combinations of the peripheral atoms (ligands).

Let us consider a triatomic BeH_2 molecule which exists only in the gaseous phase. It has a linear shape (Fig. 34). The beryllium atom acts as the central atom and the hydrogen atoms as the ligands. In beryllium, an element of the second period, the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals are valence ones (Fig. 35*a*). In hydrogen the valence orbital is the $1s$ orbital. These orbitals of the two atoms of hydrogen combine in two group orbitals (Fig. 35*b*), one consisting of $1s$ orbitals with the same signs of the wave function, and the other of orbitals with wave functions of different sign. There can be no other combinations of hydrogen orbitals in a triatomic molecule.

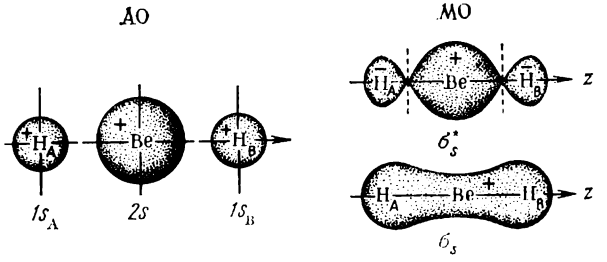


Fig. 36. Diagram of the formation of bonding and antibonding σ_s orbitals in a BeH_2 molecule

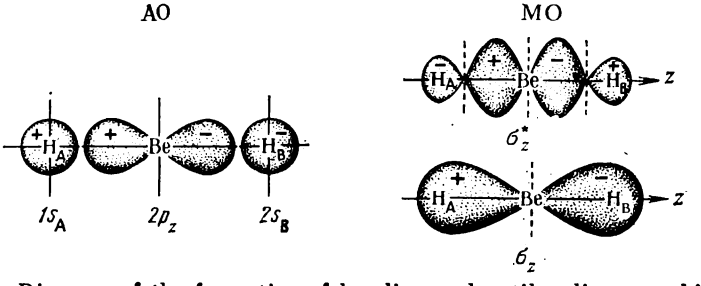


Fig. 37. Diagram of the formation of bonding and antibonding σ_z orbitals in a BeH_2 molecule

As will be seen from Fig. 35, the following combinations of orbitals of the central and group atoms are possible, given symmetry:

$$\Psi_+ (\sigma_s) \approx \psi_{2s} + \psi_1; \quad \Psi_+ (\sigma_x) \approx \psi_{2p_z} + \psi_2$$
$$\Psi_- (\sigma_s^*) \approx \psi_{2s} - \psi_1; \quad \Psi_- (\sigma_x^*) \approx \psi_{2p_z} - \psi_2$$

The first combination leads to the formation of three-centre bonding σ_s and antibonding σ_s^* orbitals (Fig. 36). A combination of $2p_z$ and ψ_2 orbitals leads to the formation of three-centre bonding σ_z and antibonding σ_z^* orbitals (Fig. 37).

As will be seen from Fig. 35, given symmetry, there are no suitable group orbitals for the $2p_x$ and $2p_y$ orbitals of the beryllium atom.

(The combination of $2p_x$, $2p_y$ orbitals and ψ_1, ψ_2 orbitals leads to zero overlapping.) The $2p_x$ and $2p_y$ orbitals are thus not involved in the formation of the molecular orbitals. They enter the BeH_2 molecule in unchanged form as *nonbonding* one-centre molecular orbitals belonging to the beryllium atom alone. The energy of electrons in nonbonding orbitals is the same (or, rather, almost the same) as in the atomic orbitals. In the symbols of the MO theory, $2p_x$ and $2p_y$ orbitals are designated πMO.

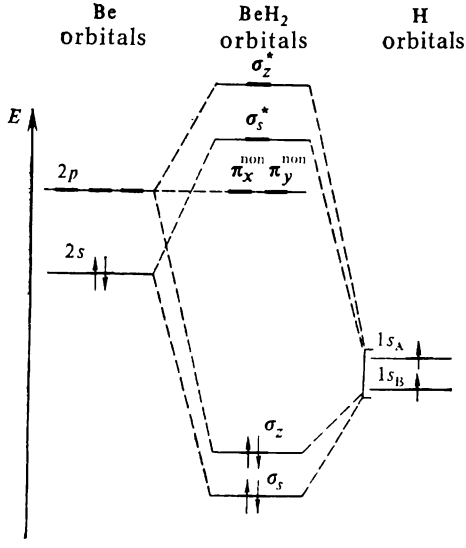


Fig. 38. Energy diagram of a linear triatomic molecule (BeH_2) without π bonding

The energy diagram of the levels of the BeH_2 molecule is given in Fig. 38. Since electronegativity of hydrogen is higher, its orbitals are below those of beryllium in the diagram. The four valence electrons of an unexcited BeH_2 molecule (two electrons from the beryllium atom and two from the two hydrogen atoms) are in σ_s and σ_z orbitals, which is described by the electron configuration

$$[\sigma_s]^2\,[\sigma_z]^2$$

The chemical bond in the BeH_2 molecule is thus ensured by two electron pairs moving in three-centre σ_s and σ_z orbitals. Each pair belongs equally to both hydrogen atoms. The order of the Be—H bond is therefore unity and the molecule's structure can be expressed by the structural formula H—Be—H, which shows that the Be—H bonds are equivalent, i.e. they are of the same length and energy.

The CO_2 molecule. The molecule of carbon dioxide is linear. Therefore, the structure of the σ MO is the same in this molecule as in the linear triatomic BeH_2 molecule. Unlike the hydrogen atom, however, the oxygen atom has p type orbitals. Consequently, there are more orbitals in the CO_2 molecule than in the BeH_2 molecule.

Figure 39 shows the valence orbitals of the central atom (carbon) and the group orbitals of the ligands (oxygen atoms), consisting of the $2p$ orbitals of oxygen. Owing to the high energy difference of the $2s$ and $2p$ orbitals of oxygen, the involvement of the $2s$ orbitals can be disregarded. Combination of the $2s$—ψ_1, $2p_z$—ψ_2 orbitals yields σ type molecular orbitals: σ_s, σ_s^* and σ_z, σ_z^* (Fig. 40).

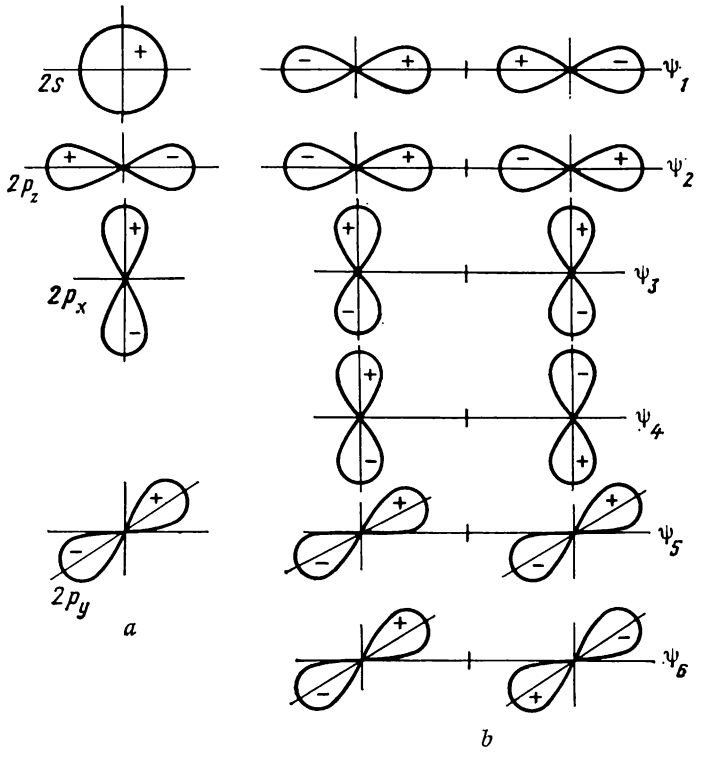


Fig. 39. Orbitals of (*a*) the central atom and (*b*) the group orbitals of a three-centre linear molecule of the CO_2 type

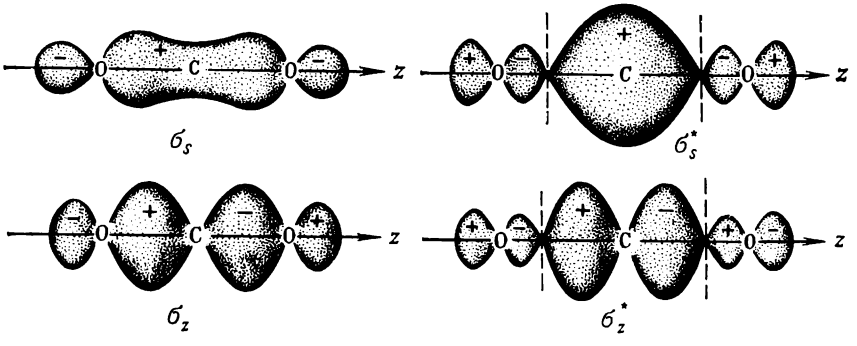


Fig. 40. Bonding and antibonding σ orbitals of Co_2 molecules

The combination of the $2p_x$—ψ_3 and $2p_y$—ψ_5 orbitals yields three-centre π type orbitals: π_x, π_x^* and π_y, π_y^* (Fig. 41). There are no symmetrically suitable orbitals of the central atom for group orbitals ψ_4 and ψ_6; therefore they act as nonbonding orbitals in the

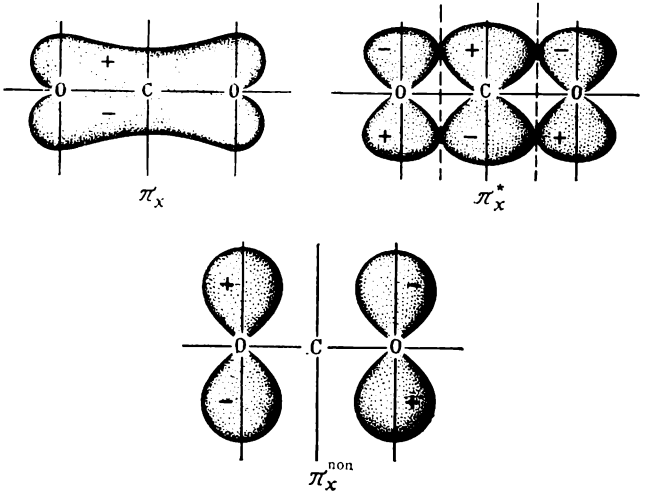


Fig. 41. Bonding, nonbonding, and antibonding π orbitals of a CO_2 molecule

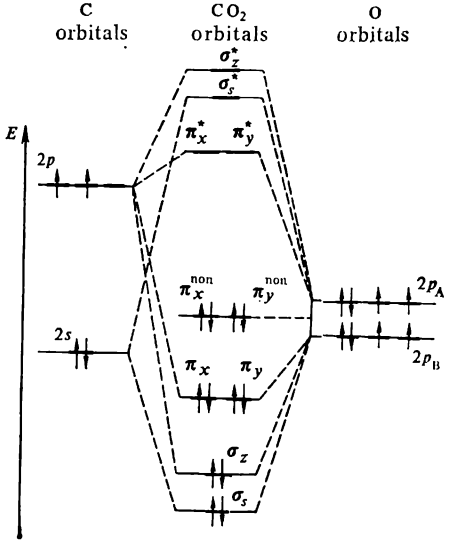


Fig. 42. Energy diagram of a linear triatomic molecule (CO_2) with π bonds

CO_2 molecule. They are designated π_x^{non} and π_y^{non}. The nonbonding orbitals are localised at the oxygen atoms.

The energy levels of the CO_2 molecules are shown in Fig. 42. The distribution of valence electrons (four electrons of the carbon atom and eight of the two oxygen atoms) in its orbitals corresponds to an electron configuration

$$[\sigma_s]^2 [\sigma_z]^2 [\pi_x]^2 [\pi_y]^2 [\pi_x^{non}]^2 [\pi_y^{non}]^2$$

and allowing for the $2s$ electrons of the oxygen atoms

$$[2s_A]^2 [2s_B]^2 [\sigma_s]^2 [\sigma_z]^2 [\pi_{x,\,y}]^4 [\pi_{x,\,y}^{non}]^4$$

The four electron pairs are distributed in four three-centre bonding orbitals, i.e. two pairs of bonding electrons per oxygen atom. The order of the bond between the oxygen and carbon atoms in the CO_2 molecule is 2, which can be shown as

$$O=C=O$$

2.5. Pentatomic Tetrahedral Molecules

The relative arrangement of the hydrogen and carbon atoms in the tetrahedral molecule of methane CH_4 is shown in Fig. 43.

As will be seen from the figure, a regular tetrahedron can be obtained if the central atom is placed in the centre of the cube and the peripheral atoms at the vertices.

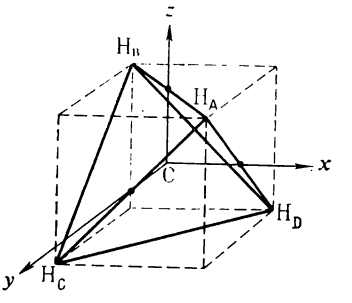


Fig. 43. Mutual arrangement of atoms in a CH_4 molecule

The $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals of the carbon atom and $1s$ orbitals of the four hydrogen atoms take part in the formation of the orbitals of the CH_4 molecule. The possible ways the valence orbitals of the carbon atom and four hydrogen atoms may overlap are shown in Fig. 44. Combination of the $2s$ orbital of the carbon atom and the $1s$ orbitals of the four hydrogen atoms (Fig. 44*a*) leads to the formation of five-centre molecular orbitals σ_s and σ_s^*. Combination of $2p_x$, $2p_y$ and $2p_z$ orbitals of carbon and $1s$ orbitals of the hydrogen atoms (Fig. 44*b*) corresponds to the formation of three σ_p [σ_x, σ_y, σ_z] and three σ_p^*[σ_x^*, σ_y^*, σ_z^*] five-centre molecular orbitals. The character of the overlapping of the $2p_x$, $2p_y$ and $2p_z$ orbitals of the carbon atom and the $1s$ orbitals of the hydrogen atoms is the same. The three σ_p molecular orbitals arising (or three corresponding σ_p^* orbitals) consequently have the same energy, i.e. they make a triply degenerate level.

The energy diagram of the orbitals of the methane molecule is shown in Fig. 45. An unexcited molecule CH_4 has two bonding and

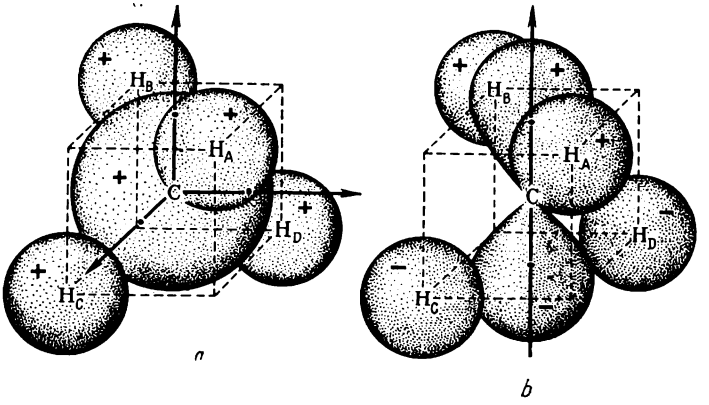
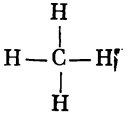


Fig. 44. Overlapping of the (*a*) 2*s* and (*b*) 2*p* orbitals of a carbon atom with the 1*s* orbitals of hydrogen in a CH_4 molecule

two antibonding energy levels. The distribution of its eight valence electrons (four from the C atom and four from the H atoms) corresponds to the following electron configuration

$$[\sigma_s]^2\,[\sigma_x]^2\,[\sigma_y]^2\,[\sigma_z]^2$$

Each molecular orbital covers all atoms of the molecule so that the four hydrogens are equivalent as regards the distribution of electron density. This corresponds to the presence of four equivalent C—H bonds which can be described by the following structural formula



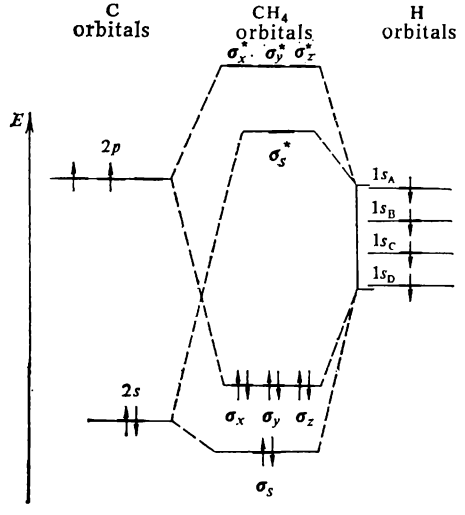


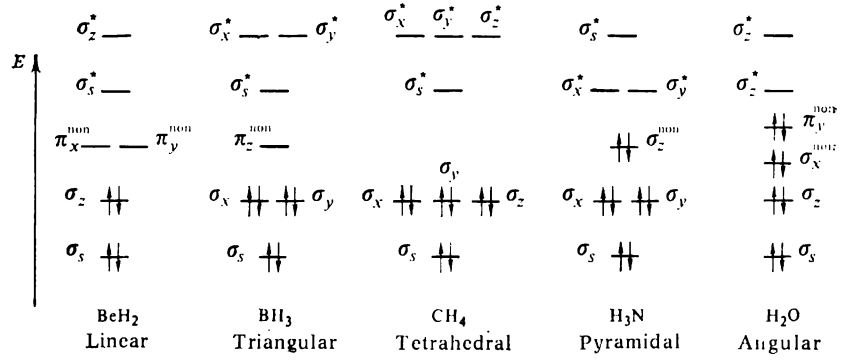
Fig. 45. Energy diagram of a tetrahedral molecule (CH_4) without π bonding.

The valence electrons are located at two energy levels (Fig. 45) so that the CH_4 molecule has *two* first ionisation potentials. Removal of an electron from the σ_s orbital requires more energy (22.1 eV) than from the σ_p orbital (13.2 eV).

It has been calculated that the 2*s* orbital of the carbon atom differs markedly in energy from the 1*s* orbital of the hydrogen atom. Therefore, for energy reasons, the combination of the 2*s* orbital of the carbon atom and the four 1*s* orbitals of the four hydrogen atoms does not yield significant overlapping; consequently the 2*s* orbital of the carbon atom in the methane molecule is nonbonding. The chemical bond in the CH_4 molecule is thus actually realised through the two 2*p* electrons of the carbon atom and the four 1*s* electrons of the four hydrogen atoms. This explanation obviously also retains the equivalence of all the four hydrogen atoms of the methane molecule and of all the four C—H bonds.

2.6. Comparison of the Energy Diagrams of Different Molecular Orbitals

It follows from comparison of the energy diagrams of linear, triangular, tetrahedral, trigonal-pyramidal, and angular molecules without π bonds



that the number of σ molecular orbitals increases in the transition from a linear to a tetrahedral molecule, while the number of π orbitals decreases. In trigonal pyramidal molecule the number of σ orbitals is the same as in triangular one but there is a nonbonding σ orbital instead of the nonbonding π orbital.

Above we have discussed the main tenets of the theory of molecular orbitals. The theory is widely employed because it provides the most general approach to all types of chemical compound. Of late it has dominated the theory of the chemical bond and theoretical chemistry in general. Its mathematical apparatus is most convenient for quantitative calculations using computers.

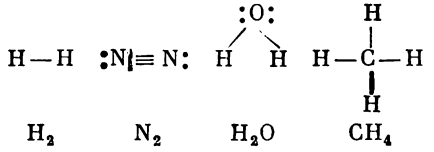
CHAPTER 3

The Theory of Valence Bonds

3.1. The Saturation of Covalent Bonds

The theory of valence bonds (localised electron pairs) assumes that each pair of atoms in a molecule is held together by one or more common electron pairs. Thus, the valence bond theory suggests that the chemical bond is localised between two atoms, i.e. it is two-centre and two-electron bond.

The designation of the chemical bond by a dash in structural formulas originated from the VB theory:



Let us consider the specific features of covalent bonds using VB theory: i.e. saturation, direction, and polarity.

One of the most important properties of a chemical bond is its *saturation*, which gives molecules a definite composition so that they exist as discrete particles with a definite structure.

Valence. By valence is meant the property of an atom of a given element to combine with or take the place of a certain number of atoms of another element. Its measure may therefore be the number of chemical bonds formed by the atom with others. So, by the valence of an element today we mean its power (in a narrower sense, the measure of its power) to form chemical bonds. The valence bond method treats the numerical value of valence as the number of covalent bonds that an atom forms.

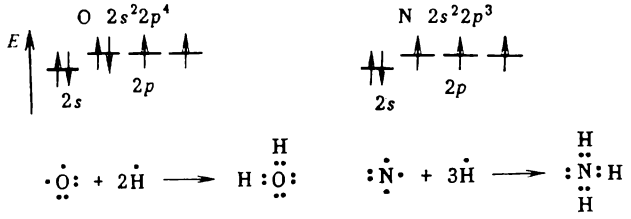
According to this theory, a chemical bond arises when two atoms with unpaired electrons meet. Overlapping of the electron clouds (single electron orbitals) of the unpaired electrons then becomes possible, so that a zone of increased electron density arises between the atoms which generates a chemical bond.

The formation of a hydrogen molecule from atoms can be described as follows (a dot is used to designate an electron while a dash stands for an electron pair):

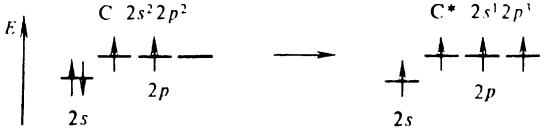
$$H\cdot + \cdot H = H:H \quad \text{or} \quad H\cdot + \cdot H = H-H$$

Since the presence of two electrons in the field of two nuclei is more advantageous as regards energy than the presence of each electron in the field of its own nucleus, all the one-electron clouds may take part in the formation of covalent bonds. For example, oxygen and nitrogen atoms can combine with two and three univalent

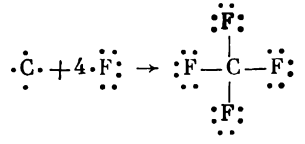
atoms of hydrogen respectively:



In some cases the number of unpaired electrons is increased owing to excitation of the atom, which breaks a two-electron cloud into two one-electron clouds. For example, a carbon atom has two unpaired electrons ($2s^2 2p^2$) in its ground state but when excited one of the $2s$ electrons in the $2p$ state gives rise to four unpaired electrons ($2s2p^3$):



As a result, the carbon atom can combine, for example, with four atoms of fluorine ($2s^2 2p^5$) having one unpaired electron:



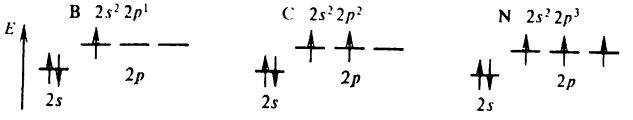
Excitation of atoms to new valence states requires expenditure of a certain amount of energy, which is compensated by the energy liberated during formation of the bonds.

The donor-acceptor mechanism of the formation of covalent (coordinate) bonds. Another mechanism of the formation of a two-centre two-electron bond is possible, viz., through the interaction of particles, one of which has a pair of electrons A: and the other an unoccupied orbital □B:

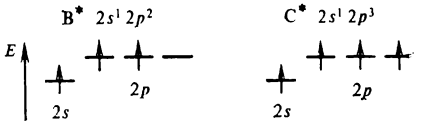
$$\mathbf{A}: + \square\mathrm{B} = \mathrm{A}—\mathrm{B}$$

The particle that donates the two-electron cloud for the bond is called the *donor* and the particle with an unoccupied orbital that accepts the pair is called the *acceptor*. The mechanism by which a coordinate (dative) bond is formed by the two-electron cloud of one atom and the free orbital of another is called *donor-acceptor*.

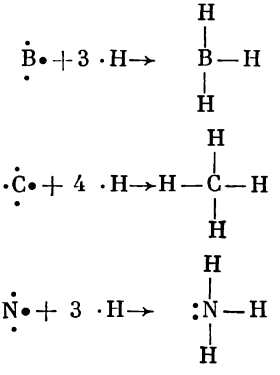
Maximum covalence. Bearing in mind that a covalent bond can be formed by two mechanisms, let us consider the valence possibility of the atoms of boron, carbon and nitrogen. These are elements of the 2nd period, hence their valence electrons are distributed in four orbitals of the outer layer: in one 2*s* and three 2*p* orbitals:



Since boron and carbon have free 2*p* orbitals of similar energy, these elements can be transformed into new configurations when excited:



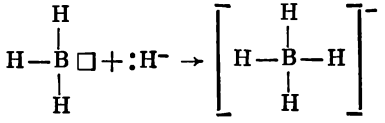
In accordance with the number of unpaired electrons, atoms of B, C and N can form three, four, and three covalent bonds respectively, for example, with the hydrogen atom:



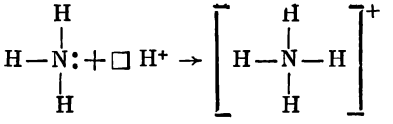
The BH_3 molecule has an electron deficit, i.e. the boron atom has a free orbital. In the H_3N molecule, the nitrogen atom has an unshared (*nonbonding*) electron pair. So the BH_3 molecule can act as the acceptor and the H_3N as the donor of an electron pair. In other words, the central atoms of both molecules can form the fourth covalent (dative) bond by the donor-acceptor mechanism.

The simplest donor is the hydride ion H^-. Attachment of a negative hydride ion to the BH_3 molecule gives a complex ion BH_4^- with

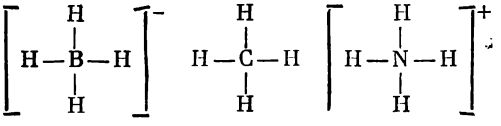
a negative charge:



The simplest acceptor is a proton H^+; its attachment to a H_3N molecule also looks to the formation of a complex NH_4^+ ion, but the charge is positive:



Comparison of the structural formulas of CH_4 and the complex BH_4^- and NH_4^+ ions



shows that the atoms of boron, carbon, and nitrogen in these compounds are tetravalent. It should be noted that all four bonds in the BH_4^- and NH_4^+ ions are equivalent, so that the charge on the ions is delocalised or spread over the whole complex.

The examples considered show that an atom's ability to form covalent bonds depends not only on the number of single-electron clouds but also on the number of two-electron clouds, or the corresponding existence of vacant orbitals.

3.2. Direction of a Covalent Bond

Since electron clouds are different in shape, they may mutually overlap in different ways. Depending on the mode of overlapping and symmetry of the resultant cloud, σ, π, and δ bonds are distinguished (Fig. 46).

Sigma bonds are formed by the overlapping of clouds along the line of connection of the atoms. *Pi bonds* arise with the overlapping of electron clouds on both sides of this line. *Delta bonds* are formed by the overlapping of all four wings of *d* electron clouds arranged in parallel planes.

Taking the symmetry conditions into account, it can be shown that the electrons of *s* orbitals can be involved in σ bonding only, *p* electrons in σ and π bonding, and *d* electrons in σ, π, and δ bonding. The modes of overlapping are even more varied with *f* orbitals.

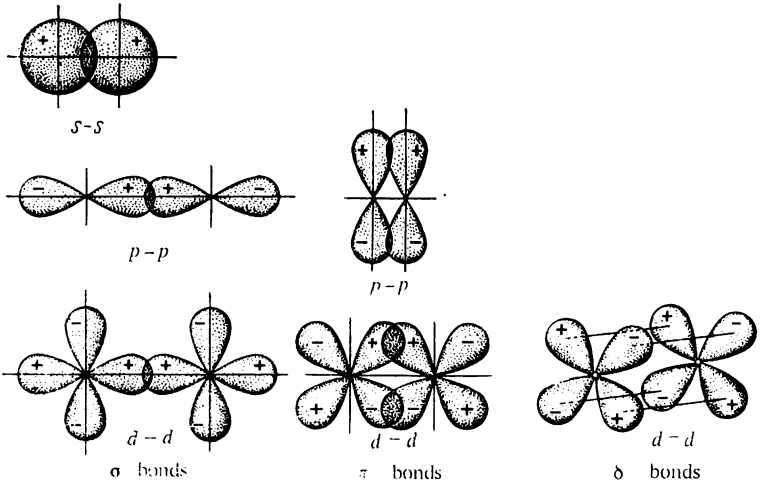


Fig. 46. Diagram of the overlapping of orbitals in the formation of σ, π, and δ bonds

The maximum overlapping of the clouds forming sigma bonds coincides with the line connecting the atom centres. Since the electron clouds (except the *s* cloud) are spatially oriented, the chemical bonds formed with their involvement are also spatially oriented. Thus dumb-bell *p* orbitals are perpendicular to each other in the atom. The bond angle formed by the *p* electrons of an atom should consequently be 90°. The spatial arrangement of sigma bonds determines the spatial configuration of molecules.

Hybridisation theory. Atoms normally form bonds by means of electrons of different energy levels. For example, *s* and *p* electrons are involved in the formation of bonds between the atoms of beryllium ($2s^12p^1$), boron ($2s^12p^2$), and carbon ($2s^12p^3$). Despite the different shapes of the initial electron clouds, the bonds formed with their involvement are equivalent and arranged symmetrically. The bond angles ClECl in the molecules of $BeCl_2$, BCl_3, and CCl_4, for example, are 180°, 120°, and 109°28′ respectively.

But how can electrons with different energy levels form equivalent chemical bonds? The answer is given by the concept of the *hybridisation of valence orbitals.*

According to this view, chemical bonds formed by the electrons are not of 'pure' orbitals but 'mixed' ones, called *hybrid* orbitals, which are the result of a mixing of atomic orbitals. In other words the initial shape and energy of the orbitals (electron clouds) are mutually altered during hybridisation and new orbitals of identical shape and energy are formed.

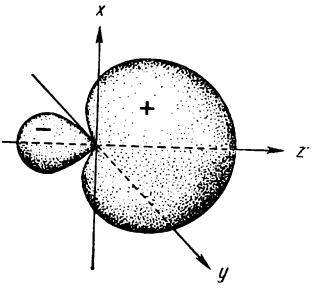


Fig. 47. Shape of an *sp* hybrid orbital

Figure 47 shows the hybrid orbital that arises from *s* and *p* orbitals. It is more elongated on one side of the nucleus than on the other and electron density is more concentrated on the one side than on the other side. Hence the chemical bond formed with involvement of the electron of a hybrid orbital must consequently be stronger than one formed by the electrons of separate *s* and *p* orbitals.

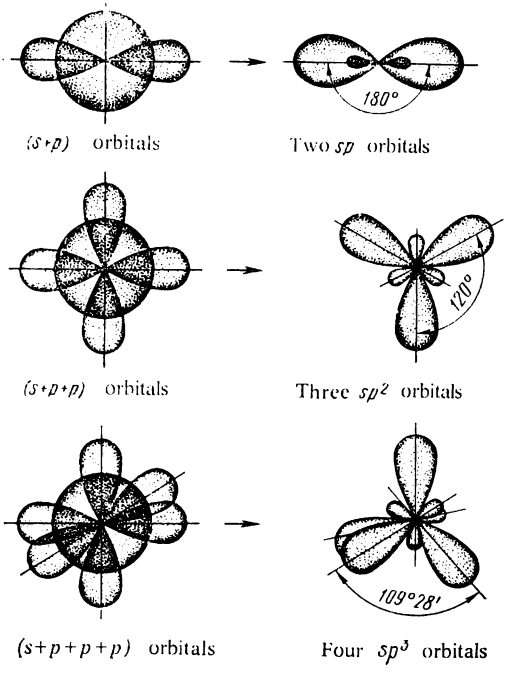
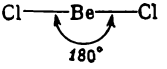


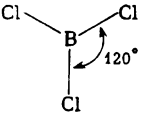
Fig. 48. Hybridisation of valence orbitals

The spatial configuration of molecules and complexes. The character of hybridisation of the valence orbitals of the central atom and

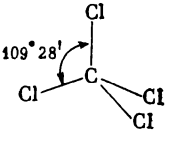
their spatial arrangement determine the spatial configuration of molecules and complex ions. A combination of one *s* and one *p* orbital yields two *sp* hybrid orbitals at an angle of 180° to one another (Fig. 48). The bonds formed by them therefore also lie at an angle of 180°. Because of *sp* hybridisation of the orbitals of the beryllium atom, the $BeCl_2$ molecule therefore has a *linear* shape:



A combination of one *s* and two *p* orbitals leads to the formation of three sp^2 hybrid orbitals at an angle of 120° to one another (Fig. 48). The bonds so formed lie at the same angle. Because of sp^2 hybridisation of the orbitals of the boron atom the BCl_3 molecule, for example, has a *triangular* shape:



A combination of one *s* and three *p* electron clouds leads to sp^3 hybridisation in which the four hybrid orbitals are located symmetrically in space at the four vertices of a *tetrahedron*, i.e. at an angle of 109°28′ (Fig. 48). A tetrahedral arrangement of the bonds is characteristic of many compounds of tetravalent carbon, e.g. CCl_4:



The NH_4^+ and BH_4^- ions have a similar structure because of sp^3 hybridisation of the nitrogen and boron atoms.

Other types of hybridisation of valence orbitals and corresponding types of spatial configuration of the molecules are also possible in addition to those considered. A combination of one *s*, three *p*, and one *d* orbital leads to sp^3d hybridisation, which corresponds to a spatial orientation of the five sp^3d hybrid orbitals at the vertices of a *trigonal bipyramid* (Fig. 49*d*). In the case of sp^3d^2 hybridisation, six sp^3d^2 hybrid orbitals are oriented toward the vertices

of an *octahedron* (Fig. 49*e*). The orientation of seven orbitals toward the vertices of a *pentagonal bipyramid* (Fig. 49*f*) corresponds to

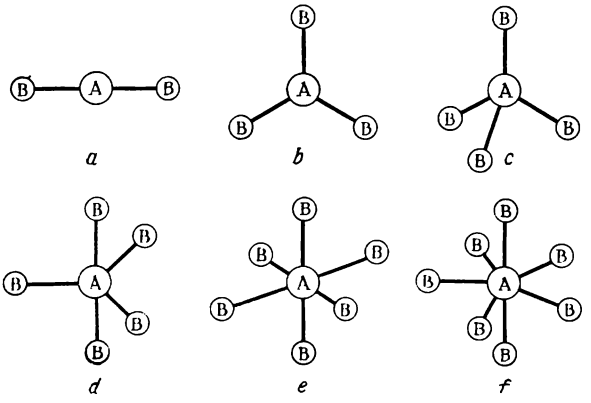


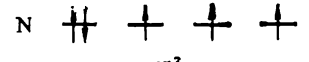
Fig. 49. Spatial distribution of bonds and configuration of molecules:
a—linear; *b*—triangular; *c*—tetrahedral; *d*—trigonal bipyramidal; *e*—octahedral; *f*—pentagonal bipyramidal

sp^3d^3 (or sp^3d^2f) hybridisation of the valence orbitals of the central atom of the molecule (complex).

The effect of a nonbonding electron pair of the central atom on a molecule's structure. We have discussed regular geometric forms of molecules and complexes with bond angles of 180°, 120°, 109.5°, and 90°. According to the experimental data, however, molecules and complexes with bond angles with rather different values are met much more often. The bond angles in H_3N and H_2O, for example, are $\angle HNH = 107.3°$ and $\angle HOH = 104.5°$ respectively. According to the theory of hybridisation, their central atoms form chemical bonds through electrons of sp^3 hybrid orbitals. In the carbon atom four electrons are distributed in four sp^3 hybrid orbitals:

This governs the formation of four C—H bonds and the arrangement of the hydrogen atoms in the methane molecule at the vertices of a tetrahedron (Fig. 50).

In the nitrogen atom five electrons are distributed in four sp^3 hybrid orbitals



Consequently one pair of electrons is nonbonding and occupies one of the sp^3 hybrid orbitals oriented toward the vertex of the tetrahedron (Fig. 50).

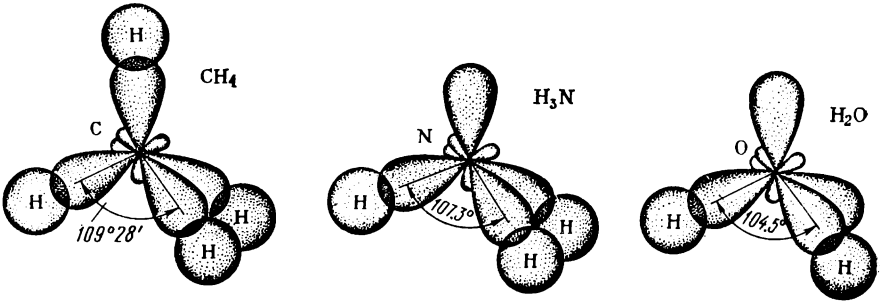
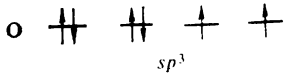


Fig. 50. Overlapping of orbitals in CH_4, H_3N, and H_2O molecules

In the oxygen atom six electrons are in four sp^3 hybrid orbitals:



Now nonbonding electron pairs occupy two sp^3 hybrid orbitals.

In terms of hybridisation theory, the decrease in the bond angle HEH in the series CH_4 (109.5°)—H_3N (107.3°)—H_2O (104.5°) is explained as follows. Since the energy difference between the $2s$ and $2p$ orbitals increases in the series C—N—O (see Fig. 11), the involvement of $2s$ orbitals in hybridisation with $2p$ orbitals decreases. This reduces the bond angle, which gradually tends to 90°.

The spatial configuration of molecules changes as the number of nonbonding electrons of the central atom increases (Fig. 51). The CH_4 molecule, for example, has the shape of a regular tetrahedron with the carbon atom in the centre (Fig. 51*a*), while in the H_3N molecule (Fig. 51*b*), one of the tetrahedron's vertices is occupied by a nonbonding electron pair so that the molecule has the shape of a trigonal pyramid. In the water molecule (Fig. 51*c*) two vertices of the tetrahedron are occupied by electron pairs, and the molecule itself has an angular (V-form) shape.

The theory of localised electron pairs. According to this theory, the arrangement of bonds and ligands around the central atom is determined by the number of its electron pairs, nonbonding ones included. The preferable arrangement of the pairs with respect to one another is their maximum separation, i.e. the minimum interorbital interaction (repulsion).

The number of the central atom's localised electron pairs and the spatial configuration of AB_n type molecules are given in Table 7 and Fig. 51. It is easy to show by means of this theory that CH_4,

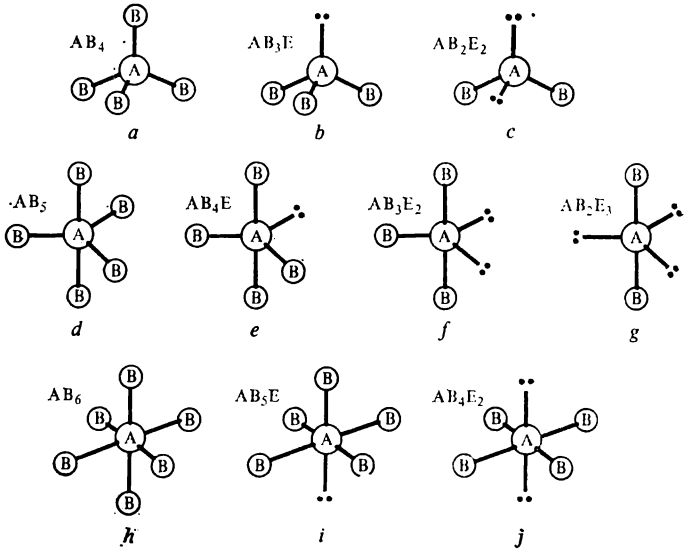


Fig. 51. Effect of nonbonding electron pairs (E) of the central atom on spatial configuration of molecules:
a—tetrahedron; *b*—trigonal pyramid; *c*—angular configuration; *d*—trigonal bipyramid; *e*—distorted tetrahedron; *f*—*T*-shaped configuration; g—linear; *h*—octahedron; *i*—tetragonal pyramid; *j*—square

H_3N and H_2O molecules belong to the AB_4, AB_3E*, and AB_2E_2* types respectively, which correspond to tetrahedral, trigonal bipyramidal, and angular spatial configurations.

A bonding electron pair (localised between two atoms) occupies less space than a nonbonding pair. Repulsion is therefore strongest between nonbonding pairs, less strong between a nonbonding and a bonding pair, and weakest between bonding pairs. The increasing number of nonbonding electron pairs of the central atom accounts for the decreasing bond angle HEH in the series CH_4 (109.5°; AB_4 type molecule)—H_3N (107.3°; AB_3E type molecule)—H_2O (104.5°; AB_2E_2 type molecule).

* E is a nonbonding electron pair.

Table 7. **Number of Localised Electron Pairs of the Central Atom and the Spatial Configuration of AB_n Molecules**

Number of electron pairs of atom A	Arrangement of the pairs	Number of σ bonding pairs	Number of non-bonding pairs	Geometrical shape and composition of the molecule *	Examples
2	Linear	2	0	Linear AB_2	BeH_2, $BeCl_2$
3	Triangular	3	0	Planar triangular AB_3	BF_3
		2	1	Angular AB_2E	$SnCl_2$
4	Tetrahedral	4	0	Tetrahedron AB_4	CCl_4, CH_4
		3	1	Trigonal pyramid AB_3E	H_3N, NF_3
		2	2	Angular AB_2E_2	H_2O, OF_2
5	Trigonal bipyramidal	5	0	Trigonal bipyramid AB_5	PCl_5
		4	1	Distorted tetrahedron AB_4E	SF_4
		3	2	T-shaped AB_3E_2	ClF_3
		2	3	Linear AB_2E_3	XeF_2, IF_2^-
6	Octahedral	6	0	Octahedron AB_6	SF_6, SiF_6^{2-}
		5	1	Square pyramid AB_5E	IF_5, SbF_5^{2-}
7	Pentagonal bipyramidal	4	2	Planar square AB_4E_2	XeF_4, ICl_4^-
		7	0	Pentagonal bipyramid AB_7	IF_7
		6	1	Distorted octahedron AB_6E	XeF_6

* E is a nonbonding electron pair.

The mutual repulsion of the bonding and nonbonding electron pairs of the central atom accounts for the effect of the nature of the peripheral atoms (or their groupings) on the size of the bond angle. In the series H_3N (107.3°) and NF_3(102°), H_2O(104.5°) and OF_2(103°), for example, the bond angle decreases. A bonding electron cloud occupies less space (is more localised) the higher the electronegativity of the peripheral atom. Since fluorine is more electronegative than hydrogen, the electron pair of the E—F bond is localised in a smaller volume than the electron pair of the E—H bond. In other words, the mutual repulsion of the electron pairs in the E—F bonds is weaker than that of the electron pairs in the E—H bonds. The repulsion of the free pairs in NF_3 and OF_2 molecules therefore decreases the bond angle more than it does in H_3N and H_2O molecules.

Multiple bonds. So far we have considered molecules with single bonds, i.e. molecules having σ bonds only. A much greater variety is found with molecules and complex ions having a bond multiplicity (order) greater than unity. The increase in the multiplicity

is due to the superimposition of π and δ bonds on the σ bond. For example, in the N_2 molecule, characterised by a triple bond

$$:\dot{\underset{\cdot}{N}}\cdot + \cdot\dot{\underset{\cdot}{N}}: \rightarrow :N \equiv N:$$

one bond is σ type, and the other two π type, corresponding to p_z—p_z, p_x—p_x, and p_y—p_y overlapping respectively (see Fig. 46).

In the linear CO_2 molecule each oxygen atom is attached to the carbon atom by one σ and one π bond: O=C=O.

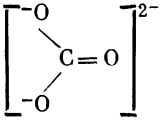
An increasing multiplicity strengthens the interatomic bond and shortens the bond length (internuclear distance). The dissociation energy of fluorine molecules F_2 ($:\ddot{F}—\ddot{F}:$) and nitrogen N_2 ($:N \equiv N:$), for example, is 159 kJ/mole and 940 kJ/mole respectively.

The effect of π bonding on bond length is well illustrated by the following series: C_2H_6—C_2H_4—C_2H_2:

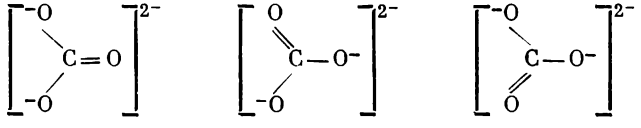
C_2H_6	C_2H_4	C_2H_2
$H_3C—CH_3$	$H_2C=CH_2$	$CH \equiv CH$

The distance between the carbon atoms decreases with an increasing bond multiplicity, and is 0.1543, 0.1353, and 0.1205 nm respectively.

A delocalised π bond. Let us consider the chemical bonds in the carbonate ion CO_3^{2-}. This ion has a triangular structure. The carbon atom forms three σ bonds through electrons of the sp^2 hybrid orbitals, the bonds lying at an angle of 120°. The fourth electron of carbon forms a π bond. Valence saturation of one oxygen atom is reached through the formation of the π bond, and of the other two by gaining an electron. The structure of this ion can be described by the following formula

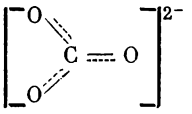


The drawback of this formula is the localisation of the π bond and the apparent nonequivalence of the C—O bond, which contradicts experiment. According to the theory of valence bonds the structure of the anion CO_3^{2-} is therefore described by three equivalent formulas rather than one:



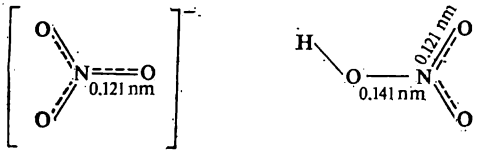
The equivalence of all bonds indicates delocalisation of the π bond (π electron cloud) and of the negative charge on all the oxygen

atoms. We can then describe the anion by one formula depicting the delocalised π electron cloud by a dotted line

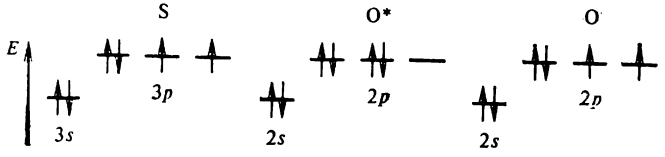


Because of the delocalisation of the π electron cloud, the bond order in C=O is about $1^1/_3$. The bond length d_{CO} in the CO_3^{2-} ion is 0.129 nm and it is intermediate between the length of the single bond d_{C-O} (0.143 nm) and the double bond $d_{C=O}$ (0.122 nm).

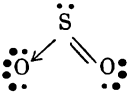
By a similar argument it can be shown that all three oxygen atoms in NO_3^- are equivalent owing to delocalisation of the charges and π bond (d_{NO} = 0.121 nm). In the HNO_3 molecule, however, one of the NO bonds is an ordinary one (d_{NO} = 0.141 nm) while the other two have the order $1^1/_3$ (d_{NO} = 0.121 nm):



The formation of bond in the molecule of sulphur(IV) oxide SO_2 can be explained as follows. The sulphur atom has two unpaired electrons, which attach one oxygen atom:



The second oxygen atom O* is combined with the sulphur atom by the donor-acceptor bond (shown by the arrow):



Since both oxygen atoms are equivalent in this molecule, its properties are best described by a structural formula with delocalised bonds:

Let us consider another example of a system with delocalised π bonds, taking the benzene molecule C_6H_6. It has the shape of a flat hexagon, and each of the six carbon atoms in the ring can be regarded as in an sp^2 hybridisation state forming three σ bonds with valence angles of 120° (Fig. 52). Three of the four

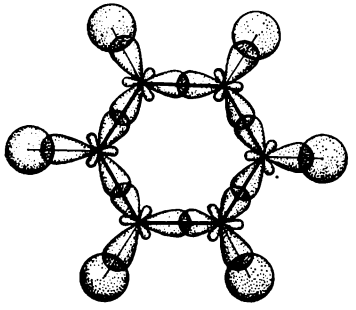


Fig. 52. Sigma bonds in a benzene molecule

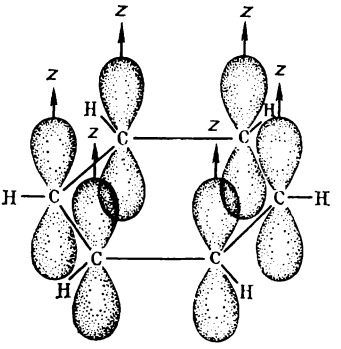
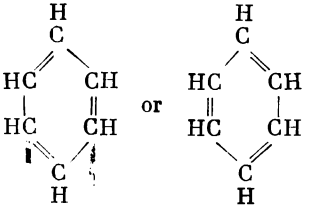


Fig. 53. Arrangement of *p* electron clouds in a benzene molecule

valence electrons of each carbon atom are involved in the formation of these three σ bonds (two C—C and one C—H bond). The other six electrons of all six carbon atoms are arranged in *p* orbitals: one electron to each carbon atom. The fourth electron cloud of each carbon atom is perpendicular to the plane of the benzene ring (Fig. 53). Two such neighbouring p_z electron clouds can overlap, forming a π bond between two carbon atoms, each cloud being capable of pairing either with the p_z cloud on its right or its left:



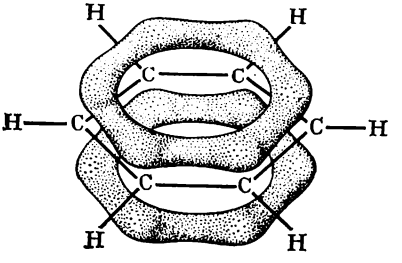
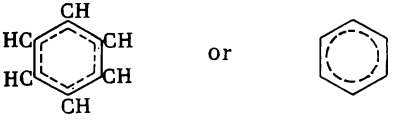


Fig. 54. Pi bonds in a benzene molecule

Consequently, we may take it that a bond arises alternatively with first the one and then the other carbon atom. In the end this leads to the formation of three single-bond electron pairs at all the carbon atoms in the benzene ring. Two fields of high electron density are formed, one on either side of the plane of the σ bonds (Fig. 54). In this bond all the carbon atoms are equivalent, and consequently such a system is more stable than one with three localised double bonds between definite carbon atoms. The chemical bonds in a benzene molecule are thus localised in the plane of the ring, and the π bonds, lying perpendicular

to that plane, are nonlocalised:



The delocalised bond in the benzene molecule accounts for the increased order of the bond between the atoms and the reduced bond length, i.e. d_{CC} is 0.139 nm in C_6H_6 while d_{C-C} is 0.1543 nm and $d_{C=C}$ = 0.1353 nm.

3.3. The Polarity and Polarisability of Bonds

The bond between the atoms of different elements is always more or less polar, due to the difference in their size and electronegativity. In a molecule of hydrogen chloride HCl, for example, the bonding electron cloud is displaced toward the more electronegative chlorine atom. As a result, the charge on the hydrogen atom is not compensated and the electron density of the chlorine atom becomes excessive compared with the nuclear charge. In other words, the hydrogen atom in HCl is polarised positively and the chlorine one negatively. A positive charge arises on the hydrogen atom and a negative on the chlorine. The magnitude of the charge δ (known as the *effective charge*) can be determined experimentally. According to the available data the effective charge on the hydrogen atom in HCl is +0.18 and that of the chlorine atom —0.18 of the absolute electron charge. The bond in the HCl molecule is 18 per cent ionic, i.e. is polar. Values of effective charges* on the oxygen atoms in oxides of elements of the third period are given below:

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Effective charge, δ_0	—0.81	—0 35	—0 31	—0.23	—0.13	—0.06	—0.01

The effective charge on the oxygen atom in Cl_2O_7 is minute and the Cl—O bond is close to nonpolar, while the effective charge on the oxygen in Na_2O is —0.81, i.e. the bond in this compound is strongly polar. The decreasing polarity of bonds in this series corresponds to the decreasing difference in the electronegativity of the elements forming these compounds. Thus a bond may be nonpolar, polar, or ionic according to the degree of displacement (polarisation) of the bonding electron cloud. Nonpolar and ionic bonds are extreme cases of polar bonds but are met less frequently.

Bond polarisability. In order to characterise the reactivity of molecules, it is important to know not only the initial distribution of electron density but also the possibility of altering it. A measure of this is bond polarisability, i.e. the bond's capacity to become

* The values of δ differ considerably when measured by different methods. The data we use here are interesting only in the sense that they illustrate the general trend in the changes of δ in a series of similar compounds.

polar (or more polar) through the effect of an external electric field on a molecule. Since an electric field is connected with each atom or molecule, a compound must also be polarised through the effect on the molecule of another molecules (e.g. reaction partners).

A bond can be completely broken by polarisation, with transfer of the bonding pair to one of the atoms and the formation of positive or negative ions. Asymmetric bond-breaking and formation of oppositely charged ions is called *heterolytic*:

$$H^{\cdot} + {\cdot}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \leftarrow H{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:} \rightarrow H^{+} + {:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{Cl}}{:}^{-}$$

Homolytic bond-breaking (dissociation) — Heterolytic bond-breaking (ionisation)

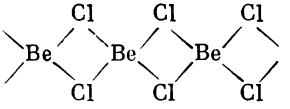
Heterolytic bond-breaking differs from the breaking of the bond when a molecule breaks down into atoms and radicals; in that case the bonding electron pair is broken apart. The process is called *homolytic*. In that connection we have to differentiate between *dissociation* and *ionisation*. In the case of HCl, dissociation occurs during thermal decomposition into atoms, and ionisation when it decomposes into ions in solution.

Oxidation number (state) of elements. By using the values of elements' electronegativity (see Fig. 15), we can make a quantitative assessment of the state of an atom in a compound in the form of its *oxidation number* or *state*, by which is understood its electric charge in a compound calculated on the assumption that the latter consists of ions.

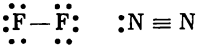
In the simplest covalent compounds, the degree of the positive oxidation state of an element is equivalent to the number of bonding electron pairs drawn from the atom, while that of the negative oxidation state is the number of electron pairs attracted to it. In the HCl molecule, for example, chlorine and hydrogen are univalent; so the oxidation state of the more electronegative chlorine (3.0) is as -1 and that of the less electronegative hydrogen (2.1) as $+1$. In molecules of ammonia H_3N and nitrogen trifluoride NF_3, nitrogen forms three bonds, i.e. is tervalent. But in accordance with the difference in electronegativity of nitrogen (3.0), hydrogen (2.1), and fluorine (4.0), nitrogen is assigned a negative oxidation state of -3 in H_3N, while its oxidation state in NF_3 is $+3$.

The use of the concept of oxidation state to characterise the state of an element is purely conventional and in most cases does not correspond to the actual character or degree of polarisation of the atom. Thus, the oxidation state of chlorine in HCl and NaCl is taken as -1, though the true polarisation (effective charge) of its atom in them is different.

In most inorganic substances the oxidation state of an element also does not coincide with the number of bonds formed by it. For example it is taken on the basis of the stoichiometric composition of $BeCl_2$, that the beryllium atom has an oxidation state of +2 and chlorine of −1. The $BeCl_2$ molecule is normally polymeric and the Be atom has four bonds, while the chlorine atom has two:



In the nonpolar F_2 and N_2 molecules the oxidation states of fluorine and nitrogen are taken as zero although the number of their bonds are one and three respectively:



In order to reflect the negative character of the polarisation of atoms in binary compounds we use the suffix *-ide* in their names, e.g. NaCl is sodium chlor*ide*, HF is hydrogen fluor*ide*, H_3N is hydrogen nitr*ide*, $FeCl_2$ is ferrous chlor*ide*, and $FeCl_3$ is ferric chlor*ide*. These binary compounds include, for example, the fluorides (NaF, CF_4), oxides (Na_2O, CO_2), chlorides (NaCl, CCl_4), nitrides (Na_3N, C_3N_4), sulphides (Na_2S, CS_2), etc.

The oxidation state of an element is a conventional concept but a very useful one. Oxidation states of elements are used to write the formulas of compounds, select coefficients for reaction equations, classify compounds, characterise their chemical nature and properties, predict the direction of chemical processes and reaction products, etc.

The highest oxidation state, with rare exceptions, corresponds to the number of the group to which the element belongs. The highest oxidation state of nitrogen (fifth group), for example, is five, of chlorine and manganese (seventh group) seven, and of xenon and osmium (eighth group) eight.

Flourine, oxygen, helium, neon, argon, and iron, and elements of the cobalt and nickel subgroups, are exceptions; their highest oxidation states are lower than the number of the group to which they belong. The highest oxidation state of elements of the copper subgroup, on the contrary, is greater than unity, although they belong to the first group.

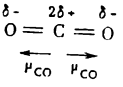
3.4. Types of Covalent Molecules

Polar and nonpolar molecules. Molecules may be polar or nonpolar depending on the distribution of electron density. In nonpolar molecules the centres of gravity of the positive and negative charges

coincide. Polar molecules are *dipoles*, i.e. the systems, consisting of two charges equal in magnitude and opposite in sign ($+q$ and $-q$), are at a certain distance l from each other. This distance between the centres of gravity of the positive and negative charges is called the *dipole length*. The polarity of a molecule, like that of a bond, is determined by the value of its dipole moment μ, which is the product of the dipole length l and the electric charge: $\mu = lq$.

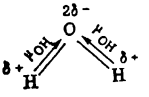
The dipole length is of the order of the diameter of an atom, i.e. 10^{-10} m, and the charge of an electron is 1.6×10^{-19} C; the dipole moment is therefore expressed by a value of the order of 10^{-29} C·m (coulomb meter)*.

The dipole moment of a molecule is the vector sum of the dipole moments of its bonds and the nonbonding electron pairs, and depends on the molecule's structure. The CO_2 molecule, for example, has a symmetrical linear structure:



Although the C=O bonds are strongly polar, the CO_2 molecule as a whole is therefore nonpolar ($\mu = 0$) because of the mutual compensation of their dipole moments. The highly symmetrical tetrahedral CH_4 and CF_4 molecules, octahedral SF_6 molecule, and so on, are nonpolar for the same reason.

In the angular (bent-chain) molecule of water, on the contrary, the polar H—O bonds are at an angle of 104.5° so that their moments are not mutually compensated, and the molecule is polar ($\mu = 0.61 \times 10^{-29}$ C·m):



The angular molecule of SO_2, the pyramidal H_3N and NF_3 molecules, and others, also have dipole moments. The absence of such a moment indicates a high symmetry of a molecule's structure while the existence of one indicates a lack of symmetry in the molecular structure (Table 8).

Nonbonding electron pairs make an appreciable contribution to a molecule's dipole moment. The H_3N and NF_3 molecules, for example, have the same trigonal pyramidal configuration, and the polarity of the N—H and N—F bonds is also about equal, but the

* The dipole moment is sometimes expressed in *Debye units* (D): 1D = $= 0.333 \times 10^{-29}$ C·m.

Table 8. **Structure and Anticipated Polarity of Molecules**

Type of molecule	Spatial configuration	Anticipated polarity	Examples
A_2	Dumb-bell	Nonpolar	H_2, Cl_2, N_2
AB	Ditto	Polar	HCl, ClF
AB_2	Linear	Nonpolar	CO_2, CS_2, $BeCl_2$ (g)
AB_2	Angular	Polar	H_2O, SO_2, NO_2
ABC	Linear	Polar	COS, HCN
AB_3	Planar triangle	Nonpolar	BCl_3, SO_3
AB_3	Trigonal pyramid	Polar	H_3N, PCl_3, NF_3
AB_3	T-shaped	Polar	ClF_3, BrF_3
AB_4	Regular tetrahedron	Nonpolar	CH_4, CCl_4, SiF_4
AB_4	Planar square	Nonpolar	XeF_4
AB_4	Distorted tetrahedron	Polar	SF_4, $TeCl_4$
AB_5	Trigonal bipyramid	Nonpolar	PF_5, PCl_5 (g)
AB_5	Square pyramid	Polar	IF_5
AB_6	Regular octahedron	Nonpolar	SF_6, WF_6
AB_7	Pentagonal bipyramid	Nonpolar	IF_7

dipole moment of H_3N is 0.49×10^{-29} C·m and of NF_3 as low as 0.07×10^{-29} C·m. This is due to the fact that the directions of the dipole moments of the bonding N—H and nonbonding electron

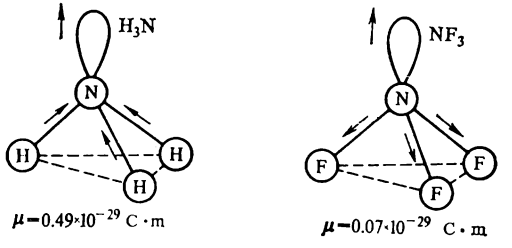


Fig. 55. Summation of the dipole moments of bonding and nonbonding electron pairs in H_3N and NF_3 molecules

pairs coincide in H_3N and with vector summation yield a large dipole moment. In NF_3, on the contrary, the dipole moments of the N—F bonds and of the electron pair are opposite in direction, so that they are partly compensated when summated (Fig. 55).

Table 9. **Dipole Moments (μ) of Selected Molecules**

Molecule	$\mu \times 10^{29}$, C·m	Molecule	$\mu \times 10^{29}$, C·m	Molecule	$\mu \times 10^{29}$, C·m
H_2	0	HBr	0.263	SO_2	0.53
N_2	0	HI	0.127	H_3N	0.494
CO	0.033	CO_2	0	H_3P	0.183
NO	0.023	H_2O	0.610	SO_3	0
HF	0.640	H_2S	0.340	BF_3	0
HCl	0.347	NO_2	0.097	CH_4	0

The dipole moments of selected molecules are given in Table 9.

Given the dipole moment, the polarity of bonds and the effective charges of the atoms can be predicted. In the simplest case of diatomic molecules, it can be taken roughly that the centres of gravity of the charges coincide with the nuclei, i.e. that l is equal to the internuclear distance or bond length. In the HCl molecule, for instance, d_{HCl} is 0.127 nm. If hydrogen chloride were a purely ionic compound (q equivalent to the electron charge) its dipole moment would have been

$$\mu = 1.6 \times 10^{-19} \text{ C} \times 1.27 \times 10^{-10} \text{ m} = 2.032 \times 10^{-29} \text{ C·m}$$

The dipole moment of gaseous hydrogen chloride, however, is in fact 0.347×10^{-29} C·m which is about 18 per cent of the calculated μ assuming that the bond is ionic. The effective charges on the atoms H and Cl in the HCl molecule are thus ± 0.18 of the electron's absolute charge.

Instantaneous and induced dipoles. A molecule is a dynamic system in which the electrons are in constant motion and the nuclei in constant oscillation, so that there can be no strictly constant distribution of charges. The Cl_2 molecule, for example, is nonpolar and its dipole moment is zero; but at any given moment the charges may shift temporarily from one chlorine atom to the other ($\overset{\delta+}{\text{Cl}} \rightarrow \overset{\delta-}{\text{Cl}}$ or $\overset{\delta-}{\text{Cl}} \leftarrow \overset{\delta+}{\text{Cl}}$) with the formation of *instantaneous microdipoles*. Since the probability of a shift of charges toward either atom is equal in both cases, the mean distribution of charges will correspond to the mean zero value of the dipole moment.

For polar molecules, the dipole moment is rather greater or less than its mean value at any given moment. The difference between an instantaneous and a permanent dipole is that the direction and value of the former vary continuously and that its direction may differ from that of the permanent dipole moment. Any nonpolar or polar molecule (or atom within it) may thus be considered as a set of instantaneous microdipoles periodically changing rapidly in value and direction.

In an external electric field a molecule is *polarised*, i.e. the charges inside it are redistributed and the molecule acquires a new dipole

moment. Nonpolar molecules may thus become polar and polar molecules even more so. In other words, an external electric field induces a dipole in molecules (called an *induced* dipole). Unlike instantaneous and permanent dipoles, induced dipoles can only exist while the external electric field generating it operates. When the action of the field ceases, the induced dipole disappears.

Intermolecular interaction is determined by the polarity and polarisability of molecules.

CHAPTER 4

Ionic Bonds. Nonvalent Types of Bonds

4.1. Ionic Bonds

The nature of the ionic bond, and the structure and properties of ionic compounds can be explained from the standpoint of the electrostatic interaction of ions. The capacity of elements to form simple ions is due to the electron structure of their atoms and can be estimated from the values of the atoms' ionisation energy and electron affinity. Cations are understandably most readily formed by elements with a low ionisation energy, i.e. the alkali and alkaline earth metals. The formation of cations by other elements is less likely in the conditions of ordinary chemical transformations, since it requires much energy to ionise the atoms.

Simple anions are most readily formed by *p* elements of group VII because of their high electron affinity. The addition of an electron to an atom of oxygen, sulphur, carbon, and certain other elements is accompanied with a liberation of energy. No addition of subsequent electrons and formation of multicharged simple anions takes place (as was shown on p. 45).

Compounds consisting of simple ions are therefore few in number and are most readily formed in the reaction of alkali and alkaline earth metals with halogens. In that case, however, the electron density between the ions is also not zero (see Table 12, p. 150), and we can therefore only speak of a *predominant* manifestation of an ionic bond. (The radii of monoatomic multicharged ions are conventional values.)

The non-directionality and non-saturability of ionic bonds. The electrical charges of ions determine their attraction and repulsion and, on the whole, the stoichiometric composition of a compound. Ions can be regarded as charged spheres whose fields of force are distributed uniformly in all directions in space. Any ion can therefore attract ions of opposite sign from any direction. In other words, ionic bonds, unlike covalent ones, are characterised by *non-directionality*.

The interaction of two ions of opposite sign cannot, of course, lead to fully reciprocal compensation of their fields of force (see

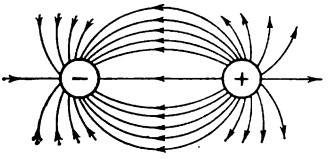


Fig. 56. Distribution of the electric fields of force of two ions with unlike charges

Fig. 56); they therefore retain their power to attract ions of opposite sign from other directions. Ionic bonds, unlike covalent ones, are also consequently characterised by *non-saturability*.

Structure of ionic compounds. Owing to ionic bonds' non-directionality and non-saturability, the best energy state is that when each ion is surrounded by the *maximum* possible number of ions of opposite sign. Because of the repulsion of like ions, however, stability of the system is achieved only with a certain mutual coordination of the ions.

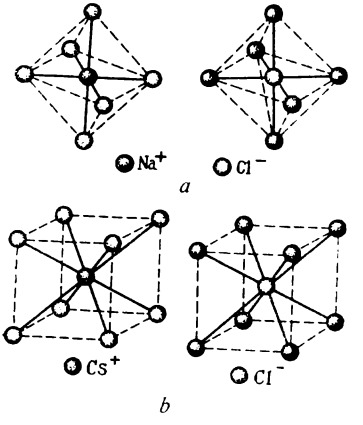


Fig. 57. Mutual coordination of ions in crystals (*a*) of NaCl and (*b*) of CsCl

In contrast to covalent compounds, the coordination number of 'purely' ionic compounds does not depend on the specific character of the electron structure of the elements but is determined by the relationship of the ions' size. If the ratio of their radii lies between 0.41 and 0.73, for example, their coordination is octahedral; if the ratio is between 0.73 and 1.37 the coordination is cubic, and so on. During the interaction of Na^+ and Cl^- ions ($r_{Na^+} = 0.098$ nm and $r_{Cl^-} = 0.181$ nm), for example, the ratio of their radii being 0.54, an octahedral coordination arises (Fig. 57*a*). The ratio of the ionic radii of Cs^+ and Cl^- ($r_{Cs^+} = 0.165$ nm and $r_{Cl^-} = 0.181$ nm) is 0.91, which corresponds to a cubic coordination (Fig. 57*b*). Such a mutual coordination of ions is achieved in the corresponding crystal lattices, viz., the simple cube of sodium chloride and the body-centred cube of caesium chloride (Fig. 58).

Thus, in normal conditions, ionic compounds are crystalline substances. The concept of simple two-ion molecules of the type of

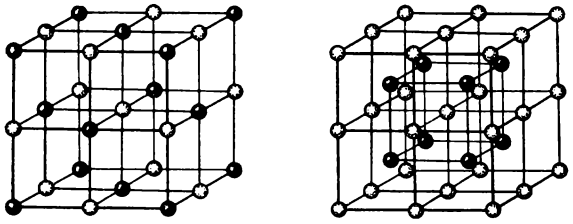


Fig. 58. Structure of NaCl and CsCl crystals

NaCl and CsCl therefore does not hold for them, and the whole crystal can be regarded as a giant molecule consisting of a huge number of $Na_n^+Cl_n^-$ and $Cs_n^+Cl_n^-$ ions.

4.2. Metallic Bonds

Important information on the nature of the chemical bonds in metals can be obtained from the two specific features distinguishing them from covalent and ionic compounds. Metals differ from all other substances, first, in their high electrical and thermal conductivity and, second, in being crystalline substances in ordinary conditions (except mercury) with high coordination numbers (see, for example, Fig. 59).

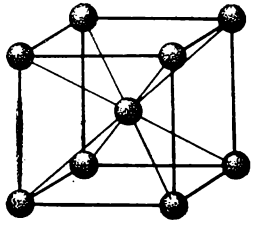


Fig. 59. Arrangement of atoms in a lithium crystal

It follows from the first property that at least some of the electrons can move throughout a piece of metal. On the other hand, it follows from the crystal structure of metals that their atoms are not linked to each other by localised two-electron bonds since the number of valence electrons in an atom is not sufficient to form such bonds with all its neighbours. Lithium, for example, crystallises in a cubic or regular body-centred lattice and each of its atoms has eight close neighbours within the crystal (see Fig. 59).

For two-electron bonds to be formed in such a structure, each lithium atom would have to furnish eight electrons, but in fact it has only one valence electron.

The nature of chemical bonding and the specific features of metals can be explained as follows taking lithium as an example. The orbitals of neighbouring atoms overlap in a lithium crystal. Each

atom provides four valence orbitals and only one valence electron for the bond, which means that the number of electrons in a crystal of the metal is much fewer than the number of orbitals. The electrons can therefore pass from one orbital to the other. The electrons are thus involved in the formation of bonds between all atoms in a metal crystal. Furthermore, metal crystals have low ionisation energies and the valence electrons are weakly held in the atom, i.e. they can move easily about the whole crystal. The possibility of this movement of electrons throughout the crystal determines the electric conductivity of metals.

Unlike covalent and ionic compounds, a small number of electrons thus simultaneously binds a large number of atomic nuclei in metals, while the electrons themselves can move about in a metal. In other words, metals have strongly nonlocalized chemical bonds. According to one of the theories, a metal can be regarded as a densely packed structure of cations connected together by a collection of shared electrons (electron gas).

Because of the nonlocalised character of metallic bonds, they are best described by the theory of molecular orbitals (see p 122).

4.3. Interactions Between Molecules

The interactions of molecules may be either electrostatic or donor-acceptor.

The electrostatic interactions of molecules are divided into orientation, induction, and dispersion interactions. *Dispersion* is the most universal type (i.e. is present in all cases) because it is due to the interaction of molecules through instantaneous microdipoles. As molecules approach one another, the orientation of their microdipoles ceases to be independent and they arise and vanish in the different molecules in rhythm with each other. Their synchronous appearance and disappearance is accompanied with attraction; in the absence of synchronism repulsion takes place.

An *orientation* (dipole-dipole) interaction is observed between polar molecules. Because of their random thermal motion they tend to become oriented. The similarly charged ends of their dipoles are repelled as they approach one another and the oppositely charged ones attracted. The stronger the polarity of the molecules, the more strongly are they attracted and so the more oriented is the interaction.

An *induction* interaction of molecules occurs through their induced dipoles. Let us suppose that polar and nonpolar molecules meet. Under the effect of the former the nonpolar molecule is deformed and a dipole is induced in it. The induced dipole is attracted to the permanent dipole of the polar molecule and in turn strengthens the electrical moment of the latter's dipole.

The greater the dipole moment and polarisability of a molecule the stronger is the induction interaction.

The relative contribution of each of these types of intermolecular force depends in the main on two properties of the interacting molecules; viz., their polarity and polarisability (deformability). The stronger the polarity, the greater is the role of orientation forces, while the greater the deformability, the more significant is the role of dispersion forces. Induction forces depend on both factors but their own role is usually secondary.

The forces of intermolecular interaction arising without transfer of electrons are known as *van der Waal's forces*. Their study is of major significance for investigating the properties and structures of gases, liquids, and solids. Van der Waal's forces are responsible for the attraction between molecules and aggregations of a substance, the conversion of a gaseous substance into a liquid and further into a solid. When gaseous chlorine is cooled, for example, crystals composed of Cl_2 molecules are formed, between which dispersion forces operate.

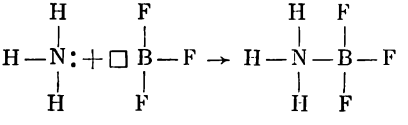
Compared with a covalent bond, van der Waals' forces are very weak. The energy required to dissociate the Cl_2 molecule into atoms, for example, is 243 kJ/mol while the energy of sublimation of Cl_2 crystals is 25 kJ/mol.

The donor-acceptor interaction. When one molecule has electron pairs, and another free orbitals, a donor-acceptor interaction can arise between them. It is displayed in the initial acts of many chemical reactions and underlies catalytic processes. It causes the solvation of molecules and ions, and in solutions can lead to the formation of many new compounds.

It is through a donor-acceptor interaction, for example, between molecules of BF_3 and H_3N that a compound (intermolecular complex) of the following composition $BF_3 \cdot NH_3$ is formed:

$$H_3\overset{\delta-}{N}\cdot\overset{\delta+}{B}F_3 \rightarrow H_3N \cdot BF_3$$

Here the positively polarised boron atom in BF_3, having a free orbital, acts as the *acceptor*, while the negatively polarised nitrogen atom in H_3N, which has a nonbonding electron pair, serves as the *donor*;



The energy of the intermolecular donor-acceptor interaction varies within a wide range of values: from 6-12 kJ/mol (which is close to the energy of van der Waals' forces) to 200-250 kJ/mol (values commensurable with the energy of ordinary interatomic covalent bonds).

Examples of intermolecular complexes are the compounds of iodine with alcohol $I_2 \cdot CH_3OH$, ammonia $I_2 \cdot NH_3$, benzene $I_2 \cdot C_6H_6$, and ether $I_2 \cdot O(CH_3)_2$. The iodine molecule acts in them as the acceptor of an electron pair (through a free π^*MO). The energy of dissociation of these molecular complexes of iodine into molecules is as low as 8-20 kJ/mol, i.e. the energy of the donor-acceptor bond is comparable to that of van der Waals' forces. The donor-acceptor bond in the complex $AlCl_3 \cdot NH_3$ is much stronger, the dissociation energy of this compound being 230 kJ/mol.

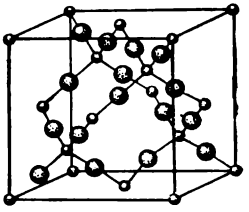


Fig. 60. Structure of the polymeric molecule (crystal) of BeF_2

The donor-acceptor interaction between molecules very often causes a substance to pass from the gaseous to the liquid or solid state. When beryllium difluoride, for example, is in the gaseous state, it has the form of linear BeF_2 molecules. Donor-acceptor relations become possible between its molecules, however, through the free orbitals of the beryllium atom and the nonbonding electron pairs of the fluorine atoms. The possibility is realised with a fall in temperature: the BeF_2 molecules associate to form a polymeric molecule Be_nF_{2n} or crystal of BeF_2 (Fig. 60), in which the beryllium atom has four covalent bonds.

4.4. Hydrogen Bonds

Experimental data indicate that the hydrogen atom can combine with two other atoms (parts of different molecules or of one):

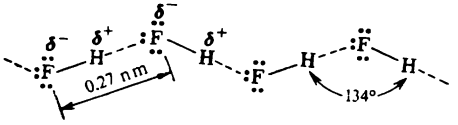
$$RA-\overset{\delta+}{H} \ldots :\overset{\delta-}{B}R_1$$

The hydrogen is usually bound much more strongly to one of the atoms (A) (because of a covalent bond) than the other (B). This latter bond is called a *hydrogen* bond and is usually depicted in formulas by a broken line or by dots.

The hydrogen bond is stronger than van der Waals' forces, its energy varies from 8 to 40 kJ/mol, but it is an order weaker than a covalent bond. A hydrogen bond is characteristic of compounds of the more electronegative elements like fluorine (25-40 kJ/mol), oxygen (13-29 kJ/mol), nitrogen (8-21 kJ/mol) and, to a lesser degree, chlorine and sulphur.

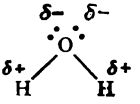
The formation of the hydrogen bond is due to the minute size of the positively polarised hydrogen atom and its power of penetrating the electron shell of a neighbouring negatively charged atom (not covalently bound with it). Consequently, there is a donor-acceptor interaction, as well as an electrostatic one, in the formation of a hydrogen bond. Hydrogen bonds are very common and

play an important role in the association of molecules and in crystallisation, dissolution, the formation of crystal hydrates, electrolytic dissociation, and other important physicochemical processes. For example, the molecules of hydrogen fluoride HF in the solid, liquid, and even in the gaseous state, are associated in zig-zag chains



which is due to hydrogen bonds.

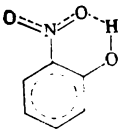
A molecule of water can form four hydrogen bonds:



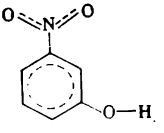
which accounts for the structure of water and ice (see p. 110).

Hydrogen bonds can lead to the formation of new chemical compounds. When aqueous ammonia, for example, is cooled, crystals of $H_3N \cdot H_2O$ (ammonium hydrate) may be precipitated. The molecules of ammonia and water are joined in this compound by hydrogen bonds.

Apart from the intermolecular hydrogen bond, there are intramolecular hydrogen bonds, as is found, for example, in orthonitrophenol:



Orthonitrophenol



Metanitrophenol

Because of this arrangement of the hydrogen bond melting point of the *ortho*-form (45°C) is lower than that of the *meta*-form (97°C), whose molecules are associated by intermolecular hydrogen bonds ($\ldots O_2N—C_6H_4—OH \ldots O_2N—C_6H_4—OH \ldots$).

In addition to inter- and intramolecular hydrogen bonds, there is also an interatomic hydrogen bond as, for example, in the HF_2^- ion: $[F \ldots H \ldots F]^-$ ($K[HF_2]$ crystal).

The hydrogen bond is strongest in this case (80-150 kJ/mol).

The hydrogen bond plays a major role in the chemistry of organic compounds, polymers, and proteins. Because of their minute strength hydrogen bonds arise and break easily at normal temperatures, which is most essential for biological processes. Hydrogen bonds, it is suggested, play a major role in the mechanism of inheritance.

CHAPTER 5

Complex Formation. Complex Compounds

5.1. Complex Formation

As we have seen, forces of attraction operate between molecules as well as between atoms, which is confirmed by the fact that interactions between molecules often lead to the formation of other, more complicated molecules. Gaseous substances, moreover, can pass into the liquid and solid states in certain conditions. Any substance is soluble in another to some extent, which is again evidence of an interaction. In all these cases there is normally a mutual coordination of the interacting particles, which can be defined as *complex formation*. It occurs, for example, in the interaction of molecules with ions, and of oppositely charged ions and molecules with each other, and so on. The ions formed during the dissolution of salts in water, for example, are hydrated, i.e. molecules of the solvent are coordinated around them. Mutual coordination of molecules is observed when substances pass from gaseous to liquid and solid states, etc.

The cause of complex formation may be either an electrostatic or a donor-acceptor interaction between ions, between ions and molecules, or between molecules.

5.2. Complex Compounds

The underlying ideas of complex compounds were introduced into chemistry by the Swiss scientist Alfred Werner (1898). The work of L. A. Chugaev and his many disciples I. I. Chernyaev, A. A. Grinberg, V. V. Lebedinsky, and others, played a big part in developing the chemistry of complex compounds. According to Werner, *inner* and *outer* spheres can be distinguished in most complex compounds. In the complex compounds $K_2[BeF_4]$ and $[Zn(NH_3)_4]Cl_2$, for example, the inner spheres consist of groupings of atoms (complexes) $[BeF_4]^{2-}$ and $[Zn(NH_3)_4]^{2+}$ while the outer spheres are K^+ and Cl^- respectively. The central atom (ion) of the inner sphere is called the *complexing agent*, while the molecules or ions coordinated around it are called *ligands*. In the empirical formulas of complex compounds the inner sphere (complex) is often placed in square brackets.

There is no generally accepted definition of 'complex compounds' because of their great variety and specific properties. In practice the chemist deals in the laboratory with compounds in the solid state or in solution. Given that, the following definition can be suggested: *compounds are called complex when there are complexes*

at the points of their crystals that are capable of an independent existence in solution. This definition, it must be stressed, by no means, of course, exhausts the essence of the problem and is applicable only within certain limits.

The classification of complexes. Complexes are classified as cation, anion, and neutral, depending on their electrical charge. In an approximation of an ionic model the charge of a complex is the algebraic sum of the charges of the particles forming it.

Cation complexes are formed by coordination of neutral molecules (H_2O, H_3N, etc.) around positive ions. The molecules of H_2O and H_3N are called aquo- and -ammine respectively in the nomenclature of complex compounds:

$[Al(OH_2)_6]Cl_3$,	hexaaquo-aluminium trichloride, or hexaaquo-aluminium(III) chloride
$[Zn(NH_3)_4]Cl_2$,	zinc tetra-ammine dichloride, or zinc(II) tetra-ammine chloride

Compounds containing *ammine* complexes are called *ammines* or *ammoniates*, and those containing *aquo* complexes *hydrates*.

In *anion* complexes the role of complexing agent is played by an atom with a positive oxidation state (i.e. a positive ion), while the ligands are atoms with a negative oxidation state (anions). The negative charge of the complex is designated by the suffix *-ate*, attached to the name of the complexing agent: for example,

$K_2[BeF_4]$,	potassium tetrafluoroberyllate(II)
$K[Al(OH)_4]$,	potassium tetrahydroxyaluminate(III)
Na_2SO_4,	sodium tetraoxysulphate(VI)
$K_2[Be(SO_4)_2]$,	potassium disulphoberyllate(II)

Neutral complexes are formed through the coordination of molecules around an atom and also through the simultaneous coordination of negative ions and molecules around a positive complexing ion: for example,

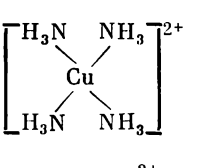
$[Pt(NH_3)_2Cl_2]$,	platinum(II) dichlorodiammine
$[Ni(CO)_4]$,	nickel tetracarbonyl
$[Cr(C_6H_6)_2]$,	chromium dibenzene

Electrically neutral complexes are therefore complex compounds without an outer sphere.

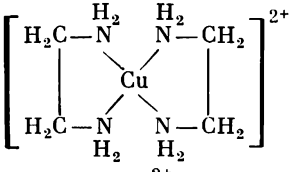
Any element of the periodic system can act as a complexing agent. Because of their chemical nature nonmetals almost always form anion complexes in which the atoms of the most electronegative elements serve as ligands, e.g. $K[PF_6]$, $K_3[PO_4]$, $K_3[PS_4]$. As for the typically metallic elements like the alkali and alkaline earth metals their capacity to form complex compounds with inorganic ligands is weak. The few complex ions of this type are cations, e.g. $[Sr(OH_2)_6]Cl_2$ and $[Ca(NH_3)_8]Cl_2$. Amphoteric elements, which occupy an intermediate position between typical metallic and

nonmetallic elements, form both cation and anion complexes like $[Al(OH_2)_6]Cl_3$ and $K[Al(OH)_4]$.

Classification of ligands. Ligands can occupy one or more places in the coordination sphere, i.e. can combine with the central atom through one or more atoms. Hence, monodentate, bidentate, tridentate, ... polydentate ligands are distinguished. Examples of monodentate ligands are the Cl^-, F^-, OH^- ions, H_3N, H_2O, CO molecules, etc. An example of a bidentate ligand is the molecule of ethylene diamine $H_2N—CH_2—CH_2—NH_2$ (*en* for short). Complexes with polydentate ligands are called chelates.* Below are nonchelate and chelate complexes of copper(II):

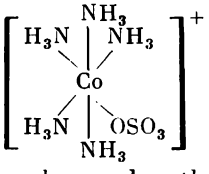


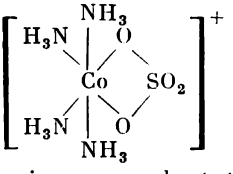
$[Cu(NH_3)_4]^{2+}$



$[Cu(en)_2]^{2+}$

The CO_3^{2-}, SO_4^{2-} ions and others like them also act as bidentate ligands:





In the left-hand complex the SO_4^{2-} is a monodentate ligand and in the right-hand one bidentate.

Many ligands can also behave as bridge atoms (or groups of atoms) in *polynuclear* (polymeric) complexes. Depending on the shape of the monatomic com-

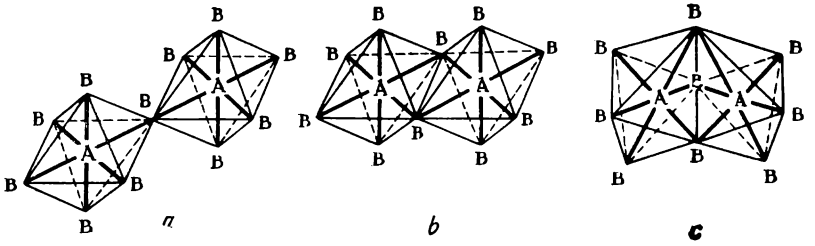
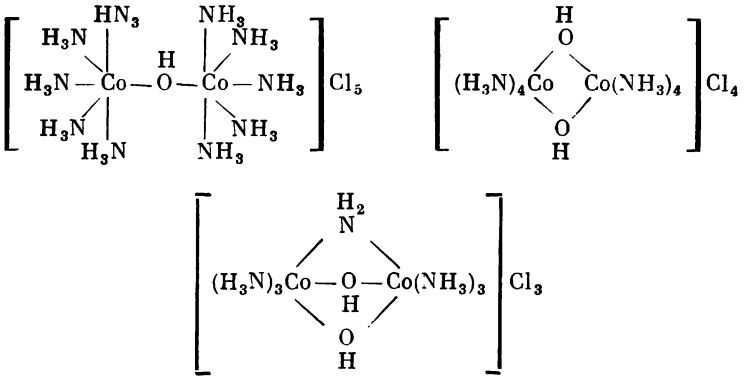


Fig. 61. Structure of binuclear complexes: octahedra joined by (*a*) one, (*b*) two, and (*c*) three bridge atoms

plexes they combine with each other in various ways. The central atoms of octahedral complexes, for example, can be joined by one, two, or three bridge atoms (or groups) (Fig. 61).

* Gr. *chēle*, claw.

Such cases of the combination of octahedrons are met, for example, in the ollowing complex compounds of cobalt (III):

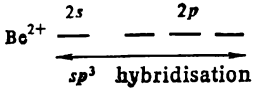


Complex compounds are common in nature and play an important role in biological processes. Suffice it to mention the chelate complexes *haemoglobin* and *chlorophyll* in which Fe^{2+} and Mg^{2+} are the complexing agents respectively. Complex compounds have many practical uses. For example, chelation (the formation of chelate complexes) is used to soften hard water and to dissolve stones in the kidneys. Complex compounds have a very important role in analytical chemistry, the production of metals, and so on.

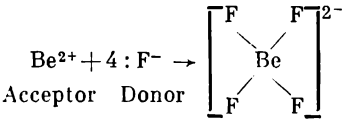
5.3. Complex Compounds from the Standpoint of Valence Bond Theory

The theory of complex compounds arose from attempts to answer the question: why many stable molecules can be coordinated around a complexing agent.

Many theories are used to explain the formation and properties of complex compounds, valence bond theory included. The main principles of the latter theory as regards complex compounds have already been discussed. According to it, complexes are formed through a donor-acceptor interaction between the complexing agent and the ligands. The formation of the tetrahedral ion $[BeF_4]^{2-}$, for instance, can be explained as follows. The Be^{2+} ion, having free $2s$ and $2p$ orbitals



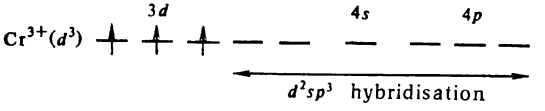
is the acceptor of four electron pairs, which are furnished by the fluoride ions:



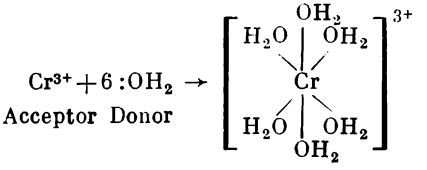
Tetrafluoroberyllate(II) ion

The tetrahedral structure of the complex ion $[BeF_4]^{2-}$ is due to sp^3 hybridisation of the valence orbitals of beryllium.

Similarly it can be shown that the interaction of the Cr^{3+} ion

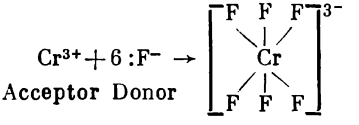


with molecules of water yields an octahedral complex ion $[Cr(OH_2)_6]^{3+}$:

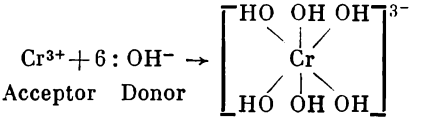


Hexaaquochromium(III) ion

The octahedral structure of this ion (see Fig. 49*e*) is governed by d^2sp^3 hybridisation of the chromium orbitals. Octahedral complexes are also formed by the interaction of the Cr^{3+} ion with fluoride and hydroxide ions



Hexafluorochromate(III) ion



Hexahydroxychromate(III) ion

The chemistry of complex compounds will be discussed in more detail in Part Two, III.

III

STATES OF AGGREGATION. DISPERSED SYSTEMS

> Nature speaks the language of mathematics. The letters of this language are circles, triangles, and other mathematical figures.
>
> Galileo Galilei

The preceding chapters have dealt with relatively simple forms of the organisation of matter, viz., atoms, ions, and molecules, but in ordinary conditions they do not exist as individual entities but always form part of a higher organisation of the matter that is involved in practice in chemical transformations, which is known as its *physical state* or *state of aggregation.*

Depending on the external conditions matter may exist in a gaseous, liquid, or solid state. The forces of attraction of the particles forming matter are electrical in nature, i.e. are directly or indirectly connected with the interaction of electrons. The transition from one physical state to another is not accompanied with a change in a substance's stoichiometric composition but is always linked with a change in its structure. In that sense, the transition may be treated as a chemical phenomenon, though one must always, of course, remember the relativity and conventionality of boundary lines, those between 'physical' and 'chemical' phenomena included.

CHAPTER 1

The Solid State

1.1. Crystals

The commonest state among solids is the *crystalline* one, which is characterised by a quite definite orientation of the particles (atoms, ions, molecules) relative to one another. This also determines the external form of matter in the shape of crystals. In the ideal case a crystal is bounded by plane surfaces, or faces, that meet at apexes

and straight edges. Single crystals (monocrystals) sometimes occur in nature; they can also be grown artificially. But most crystalline bodies are polycrystals, concretions of a large number of variously oriented fine crystals with an irregular external shape.

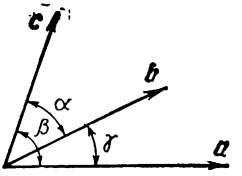


Fig. 62. Crystallographic axes

The form of crystals is studied by *crystallography*. A system of three crystallographic axes is used to describe it (Fig. 62). Unlike ordinary coordinate axes, crystallographic axes are finite lengths a, b, and c, between which there may be right or oblique angles. In accordance with their geometrical shape, the following systems of crystals occur (Fig. 63): *cubic*, *tetragonal*, *orthorhombic*, *hexagonal*, *monoclinic*, *triclinic*, and *rhombohedral*. As

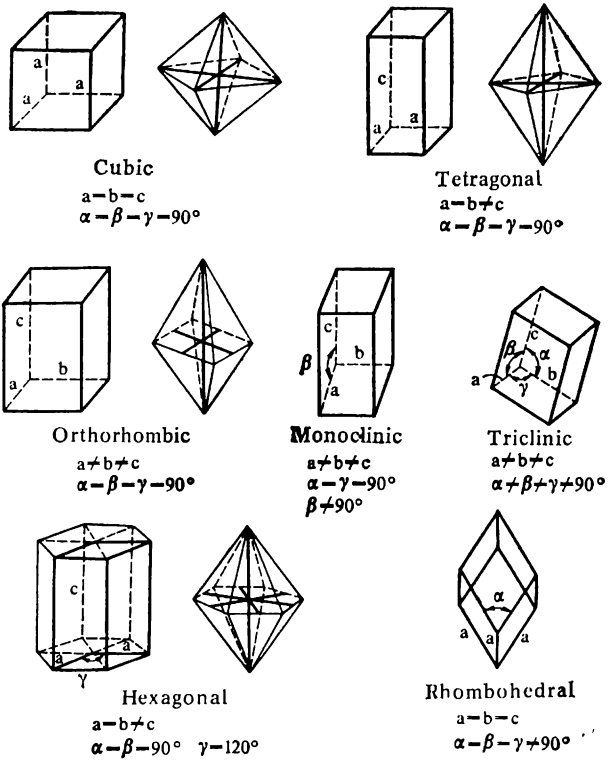


Fig. 63. The principal crystal systems

will be seen from Fig. 63, crystal systems differ in the arrangement of their crystallographic axes (α, β, γ) and lengths (a, b, c).

The symmetry of outer form reflects the symmetry of the crystal's inner structure, i.e. the regular periodic repetition of the arrangement of particles at the points of a lattice. A typical feature of crystalline bodies stemming from their structure is *anisotropy*, which is manifested in the dependence of their mechanical, electrical, and other properties on their direction in the crystal.

The particles in crystals vibrate thermally about an equilibrium position (the point of the crystal lattice). If the temperature is far from the melting point, the motion of the particles is not, as a rule, reciprocal.

1.2. Types of Chemical Bond in Crystals

In accordance with the nature of the particles a crystal lattice may be *ionic*, *atomic* (covalent or metallic), or *molecular*.

An *ionic* lattice consists of ions of opposite sign which alternate at the points. The ions can be simple (NaCl crystals) or complex (NH_4NO_3 crystals). Since the ionic bond is not saturated or directional, the structure of ionic crystals depends on the relationship between the ions' size (see Fig. 57).

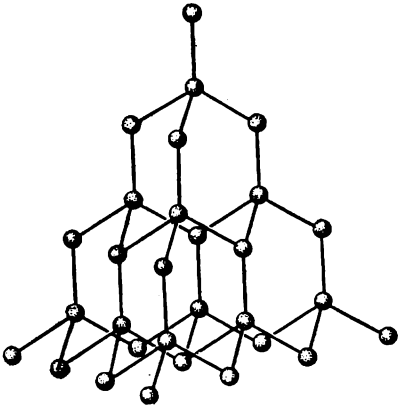


Fig. 64. The crystal lattice of diamond

In *atomic* lattices the atoms are bonded by covalent or metallic bonds. Examples of substances with an atomic-covalent lattice are diamond, and silicon dioxide, SiO_2. The structure of covalent crystals can be explained by the notion of the directionality of the chemical bond. In a crystal of diamond, for example, each atom is bonded with four neighbouring carbon atoms by electrons of the sp^3 hydrid orbitals (Fig. 64).

Atomic-metallic crystals have high coordination numbers because of their nonlocalised metallic bonds. Three types of lattice are most characteristic of them (Fig. 65): *face-centred cubic* (coordination number 12), *hexagonal* (c.n. 12), and *body-centred cubic* (c.n. eight). Copper has a face-centred cubic lattice, iron a body-centred cubic one, and magnesium a hexagonal lattice.

The points of a *molecular* crystal lattice are formed by molecules. Crystals of hydrogen, oxygen, nitrogen, the noble gases, carbon

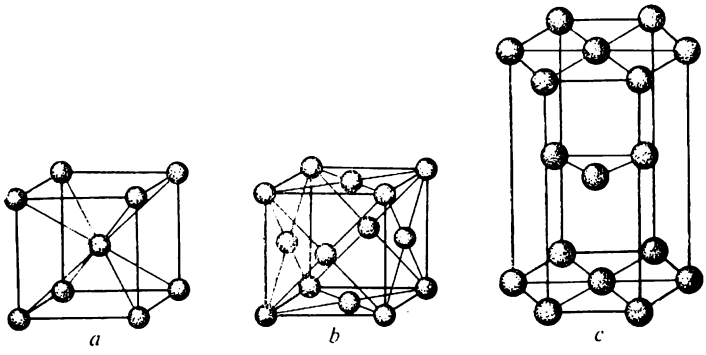


Fig. 65. Crystal lattices of metals:
a—body-centred cubic; *b*—face-centred cubic; *c*—hexagonal close-packed

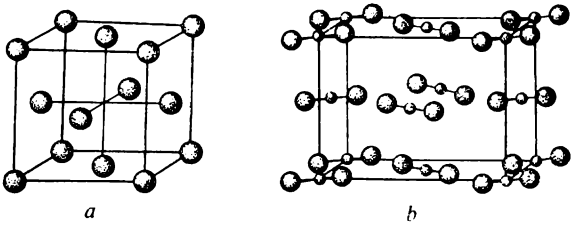


Fig. 66. Crystal lattices of (*a*) argon and (*b*) iodine

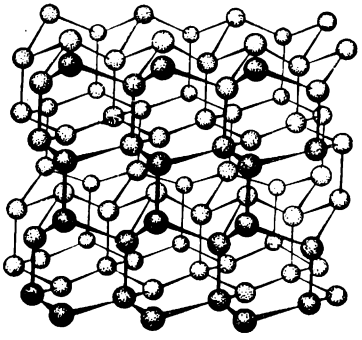
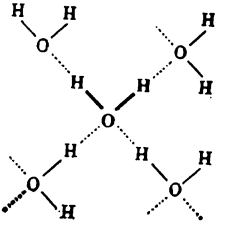


Fig. 67. Structure of ice

dioxide, and organic substances have molecular lattices. The structure of the crystals of substances with nonpolar molecules depends on the dispersion interaction. Since the dispersion forces are unsaturable and have no direction crystals with nonpolar molecules have high coordination numbers (Fig. 66). Crystals of hydrogen and helium thus have a close-packed hexagonal lattice (coordination number 12), and solid argon and iodine face-centred cubic lattices (c.n. 12).

The structure of crystals of compounds containing the atom groupings F—H, O—H and N—H is mainly determined by the hydrogen bond. The molecule of water, with two polar O—H bonds and two directed nonbonding electron pairs, can thus form four hydrogen bonds, so that each molecule in an ice crystal is therefore tetrahedrically linked with the four nearest molecules by hydrogen bonds (Fig. 67), which can be shown as follows:



Because of the tetrahedral arrangement of the hydrogen bonds an ice crystal has a diamond-like structure (see Fig. 194). And since a hydrogen bond is longer than a covalent bond, the structure of ice is quite loose and has many holes, which accounts for its low density and its capacity to form what are called *clathrate* compounds (see Fig. 136).

The various types of chemical bond in crystals account for substantial differences in the physical and chemical properties of substances with an ionic, atomic-covalent, atomic-metallic, or molecular lattice. Substances with atomic-covalent lattices for instance, are characterised by high hardness and those with an atomic-metallic lattice by plasticity. Substances with an ionic, and especially an atomic-covalent, lattice have high melting points and are not volatile. Since the intermolecular forces are weak, substances with a molecular lattice (with monoatomic, diatomic, and triatomic molecules like He, H_2, O_2, O_3, CO_2, etc.) are, on the contrary, easily fusible and volatile; their hardness, too, is low.

1.3. The Principal Structural Types of Inorganic Substances

Depending on the interatomic (interionic) distances in crystals, *insular*, *chain*, *layer*, and *coordination* structures are distinguished.

Insular, chain and layer structures. Groups of atoms can be distinguished in insular, chain and layer lattices that form isolated islands, endless chains and layers (networks) respectively. Molecules or complex ions that are joined in a crystal lattice by intermolecular or ionic bonds respectively can act as islands, chains, or layers.

Molecular lattices (see Figs. 66 and 67) and ionic lattices composed of complex ions (Fig. 68) are *insular*. The last-named act as independent structural units or unit cells and occupy corresponding points in the crystal lattice. In the crystals of $K_2[SiF_6]$ and $[Ni(NH_3)_6]Cl_2$, for example, the octahedral complex ions SiF_6^{2-} and $Ni(NH_3)_6^{2+}$ are islands (Fig. 68).

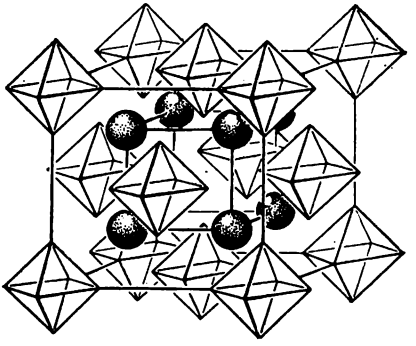
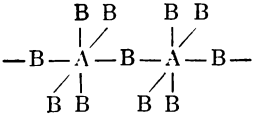


Fig. 68. Structure of compounds of the $\overset{+1}{M}_2[EHal_6]$ or $[M(NH_3)_6]X_2$ type: octahedra: SiF_6^{2-}, $TiCl_6^{2-}$, $SnCl_6^{2-}$, $Ni(NH_3)_6^{2+}$ complexes; circles: NH_4^+, K^+, Cl^-, Br^-, etc. ions

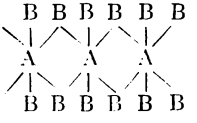
Selenium and tellurium have a *chain* molecular lattice. Graphite is an example of a substance with a *layered* molecular lattice.

Let us consider some of the types of chain and network (layer) that chemical compounds form. Let the coordination number of atom A be six, and let it combine with atoms of element B to form an octahedral group AB_6. If these octahedral unit cells are not connected with one another, an insular structure is formed, but if they are joined together the following cases are possible, depending on the way they are combined:

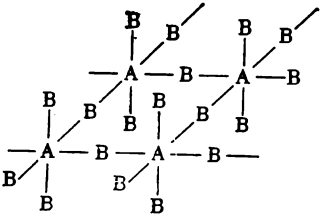
1. an octahedral AB_6 unit cell is linked with neighbours at *one* apex, forming an endless *chain* with the stoichiometric composition AB_5:



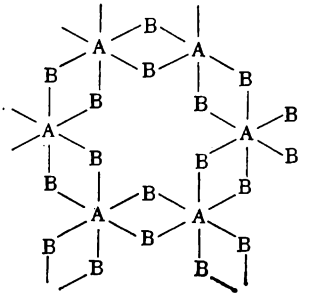
2. neighbouring AB_6 octahedra are joined at *two* apexes (or an edge), forming an endless *chain* with an AB_4 stoichiometric composition:



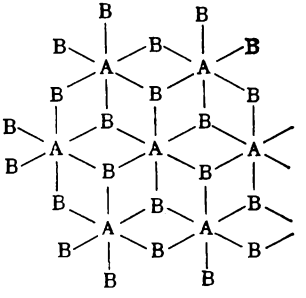
3. octahedral AB_6 unit cells are joined to *four* neighbours through their apexes in a flat two-dimensional *network* (layer) with an AB_4 stoichiometric composition:



4. octahedral AB_6 unit cells are joined to *three* neighbours by edges, forming a *layer* with an AB_3 stoichiometric composition:



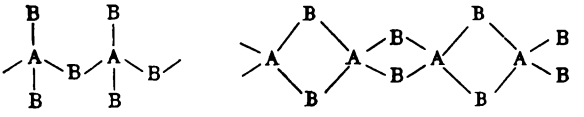
5. octahedra AB_6 are joined to *six* neighbours by their edges, forming a layer of an AB_2 stoichiometric composition:



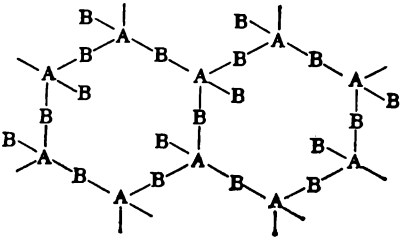
6. octahedral AB_6 unit cells are joined to *six* neighbours at *all* their apexes (i.e. in three dimensions), forming a *coordination* lattice of an AB_3 composition (see Fig. 71).

The formation of chains, layers, and coordination structures by the combination of tetrahedral AB_4 unit cells can be demonstrated

in a similar way. When AB_4 tetrahedra are joined to *two* neighbouring cells at their apexes or along an edge (two apexes), *chains* of an AB_3 or AB_2 composition are formed:



Joining of AB_4 tetrahedrat at *three* apexes leads to a *layered* structure of A_2B_5 stoichiometric composition:



If, however, AB_4 tetrahedral unit cells are joined at *four* apexes, this leads to a *coordination* lattice of AB_2 stoichiometric composition (see Fig. 70*c*).

Coordination structures. Lattices in which each atom (or ion) is surrounded by a certain number of equally spaced neighbours linked

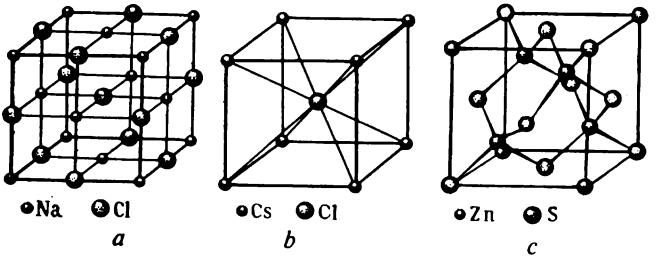


Fig. 69. The most important coordination lattices of AB type crystals: *a*—NaCl type; *b*—CsCl type; *c*—ZnS (sphalerite) type

by identical bonds (ionic, covalent, metallic) are known as *coordination*. The lattices of sodium chloride and caesium chloride considered earlier (Fig. 58), and of diamond (Fig. 64) and metals (Fig. 65), are coordination structures.

Some of the simplest and most common structural types of coordination crystals of heterochain compounds are shown in Figs. 69-72.

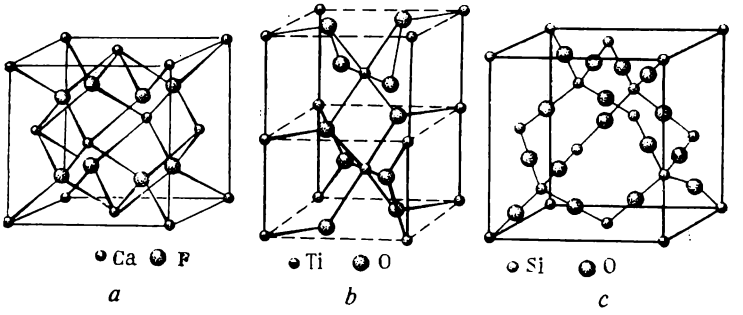


Fig. 70. The most important coordination lattices of AB_2 type crystals: *a*—fluorite CaF_2 type; *b*—rutile TiO_2 type; *c*—crystobalite SiO_2 type

In crystals of substances with an AB stoichiometric composition, the coordination numbers of the atoms (ions) are the same. The following types are most common: octahedral-octahedral (NaCl structural type, Fig. 69*a*); cubic-cubic (CsCl structural type, Fig. 69*b*); and tetrahedral-tetrahedral (ZnS structural type, Fig. 69*c*).

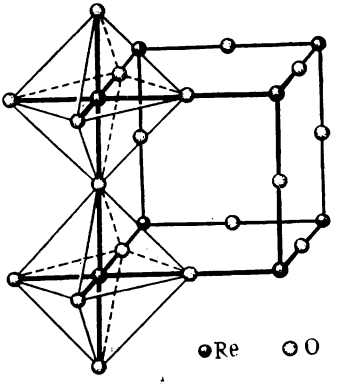


Fig. 71. Coordination lattice of compounds with an AB_3 structure (ReO_3 type)

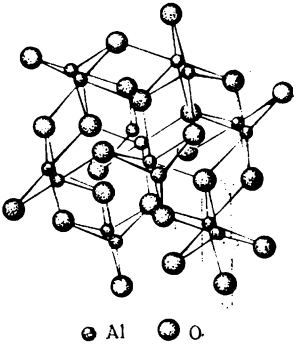


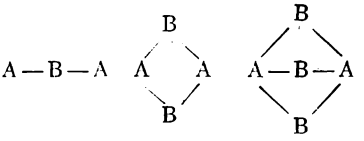
Fig. 72. Coordination lattice of compounds with an A_2B_3 structure (corundum α-Al_2O_3 type)

For substances with an AB_2 stoichiometric composition, the coordination numbers of the atoms (ions) are in a ratio of 2 : 1. The types of coordination usually observed are cubic-tetrahedral (CaF_2 structural type, Fig. 70*a*), octahedral-triangular (TiO_2 structural type, Fig. 70*b*), tetrahedral-linear (SiO_2 structural type, Fig. 70*c*).

The coordination lattices of compounds with an AB_3 composition correspond to an A : B ratio of coordination numbers of 3 : 1. Their structure usually corresponds to the ReO_3 type (Fig. 71).

In crystals of an A_2B_3 composition the coordination numbers of the atoms (ions) relate as 6 : 4, which corresponds to an octahedral-tetrahedral coordination. Their structure is usually of an alpha-Al_2O_3 type (Fig. 72).

The role of bridges (common apexes) joining unit cells into dimers, chains, layers, and trimeric networks is usually performed by the atoms of the halogens, oxygen, sulphur, nitrogen, or groups of the OH, NH_2, O_2, etc., type. Bridges can be single, double, and (less frequently) triple:



Small atoms (F, O, N) are usually involved in single bridges since the formation of double ones would lead to excess repulsion between the A atoms.

Because of the difference in the nature of bridge atoms, similar compounds of an element differ substantially in structure; for example. Be(II) and Si(IV) have a coordination number of four and a tetrahedral unit cell, but in BeF_2 and SiO_2 the tetrahedral structures are joined in a coordination crystal (Fig. 70*c*), while $BeCl_2$ and SiS_2 form chains. Al(III) and Fe(III) have a coordination number of six, but the crystals of AlF_3 and FeF_3 have a coordination lattice (Fig. 71) while $AlCl_3$ and $FeCl_3$ are layered.

The often observed difference in the properties of fluorides and oxides on the one hand and their analogous chlorides and sulphides on the other hand is therefore understandable. For example, BeF_2 and SiO_2, AlF_3, and FeF_3 are infusible, insoluble in water, and inactive chemically, while the melting points of $BeCl_2$ and SiS_2, $AlCl_3$, and $FeCl_3$ are much lower, their solubility in water and chemical activity higher.

Examples of compounds having insular, chain, layered, and coordination lattices* are given below.

Unit Cell an AB_6 Octahedron

Insular lattice

AB_6 molecule (ion) composition: SF_6, $K_2[SiF_6]$, $\overset{+1}{M}_3[FeF_6]$, $Ba_2[XeO_6]$

* Complex ions performing the role of chains, islands, or layers are given in square brackets.

Chain lattice

AB_5 chain composition: SbF_5, $Na_2[AlF_5]$, $\overset{+1}{M}_2[FeF_5]$
AB_4 composition: $CuCl_2 \cdot 2H_2O$*, $CdCl_2 \cdot 2NH_3$*

Layered lattice

AB_4 layer composition: SnF_4, $Na[AlF_4]$, $\overset{+1}{M}[FeF_4]$
AB_3 composition: $FeCl_3$, $AlCl_3$, $Al(OH)_3$
AB_2 composition: CdI_2, $MnCl_2$, $Cd(OH)_2$

Coordination lattice

AB_3 compound composition: ReO_3, AlF_3, WO_3, FeF_3
AB_2 composition: TiO_2 (rutile), MnO_2, MnF_2, GeO_2
AB composition: NaCl, FeO, MnO
A_2B_3 composition: Al_2O_3, Cr_2O_3, Fe_2O_3

Unit cell an AB_4 Tetrahedron

Insular lattice

AB_4 molecule (ion) composition: CF_4, $K_2[SO_4]$, $K_2[BeF_4]$

Chain lattice

AB_3 composition: $K[BeF_3]$, SO_3, $Na[PO_3]$
AB_2 composition: SiS_2, $BeCl_2$

Layered lattice

A_2B_5 composition: P_2O_5, $Na_2[Si_2O_5]$

Coordination lattice

AB_2 composition: SiO_2, BeF_2
AB composition: ZnS, BeO, AlAs

Unit Cell an AB_4 Square

Insular lattice

AB_4 molecule (ion) composition: $K_2[PdCl_4]$

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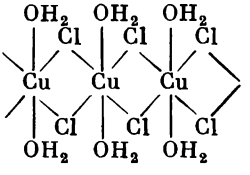
* The chlorine atoms act as bridges, for instance



Chain lattice

AB_2 chain composition: $PdCl_2$

Layered lattice

AB_2 composition: $Pd(CN)_2$

Coordination lattice:

AB composition*: PtO, PtS

Coordination lattices of three-element compounds. The structure of coordination compounds formed by three or four elements can be described by analogy with the structure of binary ones. The derivative structure of corundum, for instance (see Fig. 72), is the structure of the mineral *ilmenite*, $FeTiO_3$. The crystal of ilmenite can be regarded as a crystal of α-Al_2O_3 in which Fe and Ti atoms alternate instead of Al.

The Fe atoms can be replaced in ilmenite by atoms of Mg, Mn, Ni, Co, and Cd and the atoms of Ti by atoms of V, Nb, Rh, Mn, etc. Thus, $MgTiO_3$, $MnTiO_3$, $CoTiO_3$, $CdTiO_3$, $FeVO_3$, $LiNbO_3$, $FeRhO_3$, $CoMnO_3$, and other compounds are of the ilmenite structure type.

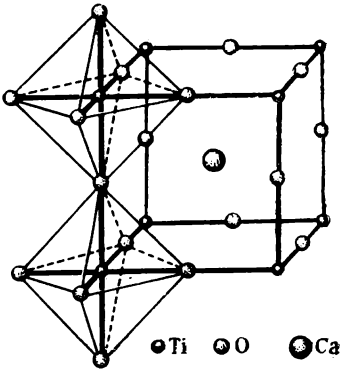


Fig. 73. Structure of perovskite $CaTiO_3$

The mineral *perovskite*, $CaTiO_3$, has a structure similar to the ReO_3 type (Fig. 71). The titanium atoms occupy the position of the Re atoms, while the Ca atoms are located at the centres of the cubic unit cells (Fig. 73). Each Ti atom in $CaTiO_3$ is surrounded by six oxygen atoms at the apexes of the octahedron and the Ca atom by twelve.

A compound of the ABX_3 type is crystallised in an ideal or distorted perovskite structure:

$\overset{+1+5}{A}\overset{}{B}O_3$ (A = Na, K, Ag; B = Nb, Ta)—$NaNbO_3$, $AgTaO_3$

$\overset{+2+4}{A}\overset{}{B}O_3$ (A = Ca, Sr, Ba; B = Ti, Zr, Ge, Sn)—$BaGeO_3$, $BaSnO_3$

$\overset{+3+3}{A}\overset{}{B}O_3$ (A = La; B = Al, Ti, Cr, Mn)—$LaAlO_3$, $LaCrO_3$

$\overset{+1+2}{A}\overset{}{B}F_3$ (A = K; B=Mg, Mn, Fe, Co, Ni, Cu, Zn)—$KMgF_3$, $KNiF_3$, $KZnF_3$

and also $\overset{+1+2}{A}\overset{}{B}Cl_3$ (A=Cs; B=Cd, Hg, Au, Ca), $\overset{+2+4}{A}\overset{}{B}S_3$ (A=Sr, Ba; B=Ti), etc.

The structure of the mineral *chalcopyrite*, $CuFeS_2$, can be regarded as a derivative of the ZnS structural type, in which atoms of Cu and Fe alternate in place of the Zn atoms (see Fig. 134).

* A square tetrahedral coordination of atoms (see Fig. 240).

Polymorphism. The crystals of a substance can differ in symmetry and shape (structure) depending on the external conditions. The ability of a substance to exist in the form of two or more crystalline structures is known as *polymorphism**. The various structural forms of the substance are called its *polymorphic modifications.*

Polymorphism is a very common phenomenon. Almost all substances can be obtained in various forms in certain conditions. A well-known example is the three allotropic forms of carbon: diamond, graphite, and carbin. The structure of graphite is layered, of carbin is a chain, and of diamond a coordinated lattice. One of the forms of ammonium chloride in normal conditions crystallises in a CsCl type of structure (coordination number eight). At high temperatures it has a NaCl type of structure (c.n. six). SiO_2 and Al_2O_3 have several variants.

Polymorphic conversions may be accompanied with substantial changes in the type of chemical bond. Diamond, for example, has covalent bonds, while graphite has covalent-metallic ones within layers and intermolecular bonds between layers.

In accordance with their differences in crystalline structure (in particular in the type of bond), polymorphous modifications also differ (sometimes very markedly) in their physical properties: e.g. density, hardness, plasticity, electrical conductivity, etc. Graphite, for example, is black, opaque, and conducts electricity, while diamond is transparent and practically a nonconductor. Graphite is soft while diamond is the hardest known substance. The density of graphite is 2.22 g/cm^3 and of diamond, 3.51 g/cm^3. Polymorphous modifications differ (sometimes very markedly) in their chemical activity.

Polymorphous modifications are usually designated by Greek letters: α denotes a modification stable at room (or lower) temperature, β denotes a modification stable at higher temperatures, and γ and δ modifications that are stable at very high temperatures. The α modification of tin, for example, with a cubic diamond-like structure, is stable at temperatures below 13.2° C while the β modification, having a tetragonal structure, is stable in normal conditions at temperatures close to melting point.

The transition from a low-temperature form to a high-temperature one is accompanied with absorption of heat; in the reverse process heat is liberated. These heat effects are called the *heat of polymorphic transformation.*

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* Polymorphism is the most widely occurring manifestation of *allotropy.* The concept of allotropy is wider than polymorphism since it refers to simple substances irrespective of their physical state (and not simply to the solid state). A notable example is oxygen/ozone.

1.4. The Characteristic Coordination Number of Elements and Structure of Their Compounds

We said earlier that oxycomplexes of a tetrahedral structure are characteristic of the nonmetallic elements of the third period in their highest oxidation states. It can be suggested that their highest oxides and polymeric oxycomplexes are also composed of EO_4 tetrahedral unit cells. The justice of this suggestion has been confirmed by experimental data on the structure of the oxides Cl_2O_7, SO_3, P_2O_5, and SiO_2, and the corresponding polymeric oxycomplexes. As will be seen from Table 10 the molecule of the chlorine(VII) oxide Cl_2O_7 is composed of two oxychlorate ClO_4 tetrahedra joined at a common apex (to an oxygen atom).

Table 10. **Modes of Combination of EO_4 Tetrahedral Unit Cells. Composition and Structure of Oxycompounds of Cl (VII), S (VI), P (V) and Si (IV)**

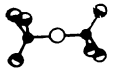
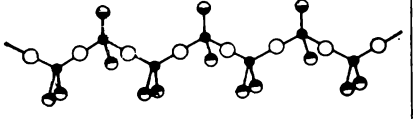
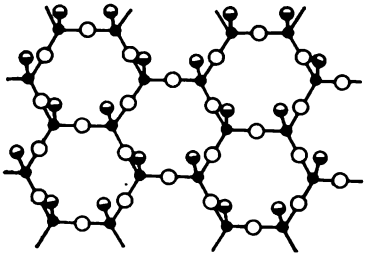
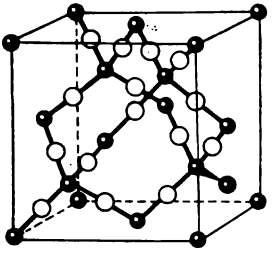
Mode of combination of EO_4 tetrahedra	Number of bridge oxygen atoms per tetrahedron	Compounds			
		Si (IV)	P (V)	S (VI)	Cl (VII)
Monomer	0	SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-
 Dimer	1	$Si_2O_7^{6-}$	$P_2O_7^{4-}$	$S_2O_7^{2-}$	$Cl_2O_7^0$
 Linear polymer	2	$(SiO_3^{2-})_\infty$	$(PO_3^-)_\infty$	$(SO_3^0)_\infty$	—

Table 10, continued

Mode of combination of EO_4 tetrahedra	Number of bridge oxygen atoms per tetrahedron	Compounds			
		Si (IV)	P (V)	S (VI)	Cl (VII)
 Layered polymer	3	$(Si_2O_5^{2-})_{2\infty}$	$(P_2O_5^0)_{2\infty}$	—	—
 Three-dimensional polymer (coordination crystal)	4	$(SiO_2)_{3\infty}$	—	—	—

In the sulphur(VI) oxide SO_4 tetrahedra furnish two apexes each during the formation of bridge bonds, which leads to a chain structure $(SO_3)_\infty$. When three apexes of the oxyphosphate PO_4 tetrahedra are used to form bridge bonds, a layered structure $(P_2O_5)_{2\infty}$ is formed. Finally, SiO_2 has an $(SiO_2)_{3\infty}$ coordination lattice because all four oxygen atoms of the silicon oxide SiO_4 tetrahedron are used to form the bridge bonds.

The complication of structure in a series of one and the same class of compounds causes a rising of the melting point and a lowering

of compounds' chemical activity. For example, in the series of oxides considered,

	Cl_2O_7	$(SO_3)_\infty$	$(P_2O_5)_{2\infty}$	$(SiO_2)_{3\infty}$
Melting point, °C	—93.4	62.2	580	1713

the melting point rises steeply and chemical activity decreases. The attitude of these oxides to water, for example, is substantially different. The reaction of Cl_2O_7 with water yields $HClO_4$. The bridge bonds in the chain structure of $(SO_3)_\infty$ break quite easily (because of its spatial accessibility) and H_2SO_4 is formed. As to the layered variant $(P_2O_5)_{2\infty}$, its reaction with water is quite complicated; only long boiling in the presence of strong acids breaks the bonds in the layered polymer with formation of H_3PO_4. The bonds of oxysilicate tetrahedra of a trimeric polymer $(SiO_2)_{3\infty}$ in practice do not break in water so that silicon dioxide hardly dissolves in water in normal conditions.

Let us consider another example, the structure of fluorides of the *p* elements of the fifth period, TeF_6, SbF_5, SnF_4 and InF_3. The characteristic coordination number of these elements is six, which corresponds to an octahedral unit cell.

The tellurium atom has six valence electrons and its coordination number of six is realised in an octahedral molecule TeF_6. Realisation of the same coordination number in the antimony atom (with five valence electrons) only becomes possible when the octahedra are joined in a polymer chain of SbF_5 composition. For tin (four electrons) it only becomes possible with the formation of a layered polymer of SnF_4 composition (see Fig. 177). Finally, the coordination number is realised for indium (three electrons) in a trimeric polymer of InF_3 composition (see Fig. 71).

The properties change significantly in this series as the structure increases in complexity. In normal conditions TeF_6 is a gas, SbF_5 is viscous liquid, while SnF_4 and InF_3 are crystalline substances melting at 400 °C and 1170 °C respectively. The increasing complexity also accounts for these substances' decreasing solubility in water and weakening of chemical activity.

As already indicated, the characteristic coordination numbers of elements increase in subgroups with rise in atomic number. The structure of compounds, and hence their properties, are therefore different with one and the same stoichiometric composition. Let us consider the series of dioxides of *p* elements of group IV (CO_2, SiO_2, GeO_2, and SnO_2). The characteristic coordination number of carbon(IV) is two, of silicon(IV) four, of germanium(IV) four and six, and of tin(IV) six. Thus only the composition of carbon dioxide corresponds to the characteristic coordination number of the central atom, so that CO_2 is monomolecular. As for the other dioxides, their stoichiometric coefficients differ from the stable

coordination numbers of the central atoms, so that the compounds are polymeric. The coordination crystals of one of the GeO_2 variants belong to the SiO_2 type (Fig. 70*c*) and those of the other variant to the rutile type TiO_2 (Fig. 70*b*). The crystals of SnO_2 also have a rutile type of structure.

1.5. The Band Theory of Crystals

Energy bands. The band theory of crystals, which treats solids as a single group of interacting particles, gives a general approach to considering ionic, covalent, and metallic crystals. It is a theory of molecular orbitals for systems with a very large number ($\sim 10^{23}$) of atoms.

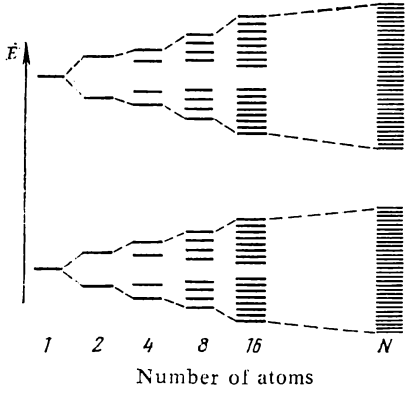


Fig. 74. Structure of energy bands with successive joining of atoms

In the concepts of the theory of molecular orbitals there is an overlapping of atomic orbitals during the interaction of two atoms, with the formation of bonding and antibonding molecular orbitals, and each atomic energy state is split into two molecular states (in a system of four atoms into four, in a system of eight atoms into eight, and so on). The more atoms there are in a system the more molecular states there are. If a crystal is formed from N atoms, each atomic energy state will be shifted as regards energy and split into N states (Fig. 74). Since N is very large (one cubic centimetre of a metallic crystal may contain between 10^{22} and 10^{23} atoms!), the N levels are very close to one another, forming an *energy band*. The energy difference of the electron states within a band is only 10^{-22} eV, so that the change in an electron's energy can be represented as a continuous zone of energy. The orbitals of the energy band can be regarded as analogues of molecular orbitals extending throughout the crystal.

The formation of energy bands in a crystal from the energy levels of its atoms as they approach one another is shown in Fig. 75. Suppose that the atoms are arranged at the points of a lattice with bond lengths many times greater than those in the lattice of a real crystal. The energy levels of this hypothetical crystal are the quantum states of the separate atoms. As these are brought closer to one another, this state corresponds to their interaction and the transformation of their energy levels into energy bands. The width and

position of the energy bands are determined by the equilibrium distance r_0 between the atoms.

The orbitals of an energy band are filled with two electrons in the same way as those of the atom and molecule, i.e. in accordance with Pauli's principle, in the order of their arrangement by energy. Consequently, the maximum possible number of electrons in the bands resulting from the overlapping of s, p, d, and f atomic orbitals is $2N$ (s band), $6N$ (p band), $10N$ (d band) and $14N$ (f band), and so on. The band occupied by the electrons effecting the chemical bond is called the *valence* band (the shaded zone in Fig. 75), while the free zone above it is called the *conduction* band.

Depending on the structure of the atoms and the symmetry of the crystal lattice, the valence and conduction bands may overlap (Fig. 75*b*) or may not (Fig. 75*a*). The energy gap formed between them in the latter case is called the *forbidden* band.

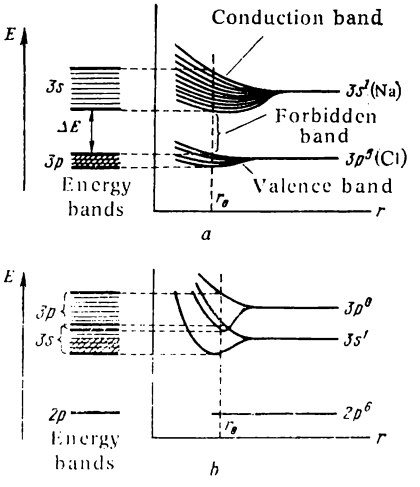


Fig. 75. Formation of energy bands in a crystal from the energy levels of atoms as they become closer together: *a*—bands do not overlap; *b*—bands overlap

In accordance with the way the bands are arranged and filled substances may be either *dielectrics* (insulators), *semiconductors*, or *conductors* (metals). The forbidden band ΔE of dielectrics is over 3 eV wide and in semiconductors between 0.1 and 3 eV. In metallic crystals, because of overlapping of the valence and conduction bands, there is no forbidden band.

Let us now consider the way the energy bands of metallic, covalent, and ionic crystals are filled.

Metallic crystals. Elements like sodium and copper have only one s valence electron, so that the valence band built from s atomic orbitals is only half-filled in crystals (Fig. 75*b*). It therefore follows that even slight excitation can alter the energy state of each electron over the whole range of the energy band. This happens, for example, when an electric field is applied to a metal: the electrons receive additional energy and begin to move in the direction of the field, which determines electrical conductivity in metals.

In elements with two valence electrons, the s zone is filled to capacity. If the s and p levels are close to one another in isolated atoms, however, the corresponding energy bands in crystals overlap,

so that here too the number of valence electrons is not sufficient to fill the energy levels of the overlapping bands.

Metallic crystals are thus formed by elements in which the number of valence electrons is small compared with the number of valence orbitals close in energy to one another. Consequently the chemical bond arising in metallic crystals is highly delocalised.

Covalent crystals. We shall consider the filling of the energy bands of a covalent crystal on the example of diamond in which the width of the forbidden band is $\Delta E = 5.7$ eV. The electrons of carbon atoms fill the valence band to capacity. Since the transition of electrons from the valence band to the conduction band requires high excitation energy (which cannot be applied to diamond in ordinary conditions), diamond remains a dielectric.

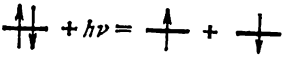
The structure of crystalline silicon is the same as that of diamond, so that the valence band of a silicon crystal is also completely filled. But the width of the forbidden band in this case is only $\Delta E = 1.12$ eV, so that valence electrons can be excited to the conduction band by a lower energy, i.e. silicon is a semiconductor.

Ionic crystals. In a crystal of sodium chloride (Fig. 75*a*) the valence electrons of the sodium atoms ($3s^1$) and chlorine atoms ($3s^23p^5$) fill the valence band $3p$. In the concepts of ionic bond theory, this corresponds to the transition of electrons from the sodium atoms to the chlorine atoms and the formation of Na^+ and Cl^- ions. Since the energy difference between the valence $3p$ band and the free $3s$ band is great ($\Delta E = \sim 6$ eV), NaCl does not possess electron conductivity in ordinary conditions.

Molecular crystals. In molecular crystals the molecules are linked through electrostatic intermolecular forces, and the energy levels are localised within the molecules. In ordinary conditions there is no transfer of electrons between the molecules.

1.6. Semiconductors

As we have seen, comparatively little energy is required to transfer electrons from the valence band to the conduction band in semiconductors. This happens when the bond formed by a pair of electrons is broken through absorption of an energy quantum (heating or illumination). One of the electrons is transferred to the conduction band so that only one remains at the energy state of the valence band, i.e. a positively charged vacancy, known as a hole, is formed:



Valence band — Hole in valence band — Electron in conduction band

If an electric field is applied, the electrons in the conduction band will move toward the anode, while the electron in the valence band nearest to the hole moves to the freed place to form a new hole into which the next electron moves, creating another hole, and so on (Fig. 76). This drift of electrons is equivalent to a drift of the holes in the opposite direction, i.e. toward the cathode. The conduction of electricity in semiconductors is thus brought about both by the electrons transferred to the conduction band and the holes in the valence band, i.e. both *electron* (*N*-type) and *hole* (*P*-type) conductivity occurs.

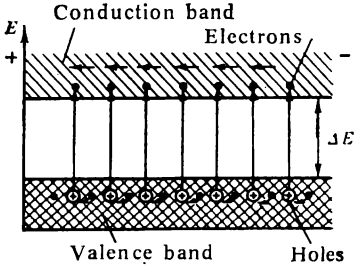


Fig. 76. Band diagram of the intrinsic conductivity of a conductor

The number of electrons transferred to the conduction band, and hence the number of holes, increases as the temperature rises or illumination increases, which explains the specific difference between semiconductors and metals: in the former conductivity increases substantially with a rise in temperature, while it falls in metals.

At absolute zero, in the absence of other external influences, the electrons in semiconductors do not have enough energy to overcome the forbidden band. In these conditions therefore semiconductors become dielectrics. It follows, consequently, that the division of substances into semiconductors and dielectrics is quite conventional. The wider the forbidden band, the higher the temperature that is required to induce electron-hole conductivity.

The ratio between the number of electrons and the number of holes can vary if semiconductors contain impurities, i.e. either electron or hole conductivity may prevail. Let us suppose that a silicon crystal contains an admixture of arsenic ($4s^24p^3$). During the formation of bonds with surrounding atoms, the arsenic atoms use up four of their electrons. The fifth electron is quite easily excited and crosses to the conduction band. Thus an admixture of arsenic increases electron conductivity in silicon. Conversely, the introduction of boron atoms ($2s^22p^1$) into a silicon crystal leads to valence non-saturation in the silicon atoms, i.e. increases hole conductivity in the semiconductor.

Structural defects in crystals also affect the electrical conductivity of semiconductors, usually inducing hole conductivity. Depending on which type of conductivity prevails, *n*-type and *p*-type semiconductors are distinguished.

All crystals with nonmetallic bonds have semiconductor properties but these are most pronounced in substances with covalent bonds

of low energy. In ordinary conditions semiconductor properties are observed in such simple substances as silicon, germanium, selenium, tellurium and boron. Among complex compounds, those with a diamond-like crystal lattice present special interest.

CHAPTER 2

The Liquid State

2.1. The Structure of Liquids

The forces acting between the particles of substances in the liquid state are strong enough to hamper their random motion but not sufficiently strong to suppress their motion relative to one another.

Like solids, liquids have a definite structure. The structure of liquid water, for example, resembles that of ice: the H_2O molecules are also held together by hydrogen bonds and most of them preserve a tetrahedral configuration. Unlike ice, however, liquid water displays only short-range order (because of bending and stretching of the hydrogen bonds, the arrangement of the tetrahedral unit cells relative to one another is random). Owing to the motion of the molecules, moreover, some of the hydrogen bonds are broken and the composition of the unit cells changes constantly. The incessant motion of the particles accounts for the very marked self-diffusion and mobility of the liquid. The concept of a liquid as a disordered solid was introduced by a Soviet scientist, Ya. I. Frenkel.

The liquid state is intermediate in structure between solids, which have a definite periodic structure throughout the crystal (i.e. long-range order) and gases, in which there is no structure of any kind and the motion of the particles is random.

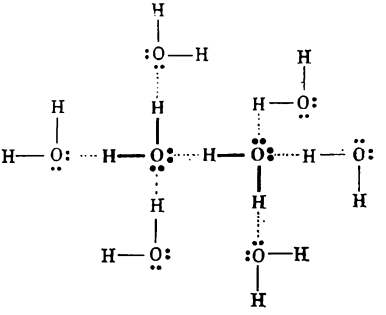
Hence a definite volume is typical of liquids on the one hand and, on the other hand, absence of definite shape. The first circumstance allies them with solids and the second with gases. As the temperature of a liquid nears freezing point its internal structure becomes much more regular, but as it approaches boiling point, the mutual arrangement of the particles becomes random.

The structure and physical properties of a liquid depend on the specific chemical properties of the particles forming it, and on the character and intensity of the forces acting between them. In water, as we have seen, hydrogen bonds play a major role in the association of molecules in complexes. With nonpolar molecules, the interaction and mutual position of the molecules depend on dispersion forces, and since these are non-saturated and non-directional, liquids with nonpolar molecules also have high coordination numbers.

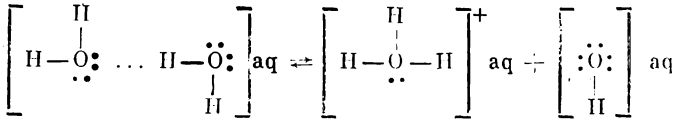
High coordination numbers are attained in liquid metals as well since metallic bonds are also unsaturated and non-directional. In other words, the general patterns observed in the formation of complexes (unit cells) are the same for liquids and solids. The difference is the absence of rigidity of structure and of long-range order in the arrangement of particles.

2.2. Ionisation of the Molecules of Liquids

The features of the structure of liquids considered above, and the ability of molecules to move relative to one anoter, predetermine whether they can be ionised. Let us take the behaviour of water molecules in neighbouring tetrahedral complexes as an example (printed in bold type):



These molecules lie in the field of action of neighbouring molecules and are linked to them by hydrogen bonds. In addition, they mutually affect each other. The thermal motion of the particles within a complex, and the movement of the complexes in relation to one another, can weaken the O—H bond in one of the molecules and break it, which is accompanied with transfer of the proton to a neighbouring molecule through transformation of the hydrogen bond into a covalent bond on the donor-acceptor principle:



or

$$H_2O \cdots HOH \rightleftharpoons OH_3^+ + OH^-$$

As a result of ionisation of the H_2O molecules, hydrated ions OH^- and OH_3^+* arise. When they collide, a molecule of water is

* The probability of existence of a non-hydrated H^+ ion in an aqueous solution is $1 : 10^{150}$.

again formed, i.e. the ionisation process is reversible. Ionisation and molisation go on continuously. Because of the strength of the O—H bond, the degree of ionisation of water in general is slight.

A similar picture of self-ionisation is met in other liquids whose molecules are linked by hydrogen bonds, for example:

$$H_3N \ldots HNH_2 \rightleftharpoons NH_4^+ + NH_2^-$$
$$H_2S \ldots HSH \rightleftharpoons SH_3^+ + SH^-$$
$$HNO_3 \ldots HNO_3 \rightleftharpoons NO_3H_2^+ + NO_3^-$$
$$H_2SO_4 \ldots HSO_4H \rightleftharpoons SO_4H_3^+ + SO_4H^-$$

In these examples, transfer of a proton from one molecule to another also takes place, so that negative and positive ions are generated surrounded by a shell of nonionized molecules. Generally these ions are said to be *solvated.* Ions of the type of OH_3^+ and NH_4^+ are known as *lyonium ions* (*oxonium*, *ammonium*). Ions of the OH^-, NH_2^-, SH^- and NO_3^- type are called *lyate ions.*

Thus it can be seen that during ionisation, one of the interacting molecules is the donor of electron pairs and the other the acceptor.

Substances that act in chemical reactions as donors of electron pairs are *bases*, while acceptor substances are *acids.* In our examples the donor-acceptor interaction occurs through proton transfer, so that basic properties are displayed by the molecules that gain a proton and acid properties by those that donate one. Reactions accompanied with transfer of a proton are called *protolytic.*

In some reactions the donor-acceptor interaction is effected through the transfer of some other ion, e.g. F^- or Cl^-:

$$\underset{\text{Donor}}{BrF_3} + \underset{\text{Acceptor}}{BrF_3} \rightleftharpoons BrF_2^+ + BrF_4^-$$

These reactions are known as *aprotic.*

The basic and acidic properties of a substance are only two aspects of a single process of acid-base interaction. Acidic properties are displayed only during interaction with substances having basic properties, and vice versa. Substances that display both acidic and basic properties (i.e. are capable of donating and accepting electrons) are called *amphoteric.* In the examples above, liquid H_2O, H_3N and HNO_3 are amphoteric compounds.

The degree of ionisation of a substance in the liquid state depends on the strength of its molecules and the character and intensity of the intermolecular interaction. Substances with stable covalent nonpolar molecules (e.g. liquid O_2, Cl_2, CF_4, etc.) have the lowest degree of ionisation. In substances with an ionic structure (since they already consist of ions) liquefaction or fusion leads only to disruption of their crystal lattice and movement of the ions relative to one another.

2.3. The Amorphous State

X-ray studies show that the amorphous state is similar to the liquid state, i.e. is characterised by no definite order in the mutual arrangement of particles. Figure 77 shows the structure of vitreous silicon dioxide. As will be seen, the ordered arrangement of unit cells characteristic of crystalline SiO_2 (see Fig. 70*c*) does not hold rigorously for the vitreous variant. As a result, the separate bonds between the unit cells are not equivalent. Amorphous substances do not therefore have definite melting points: as they are heated, they soften gradually and melt. The temperature range of this process for silicate glass, for example, is 200 °C. In crystalline bodies, at the melting point long-range order disappears and only short-range order remains. In amorphous substances the character of arrangement of the atoms hardly changes with heating, only mobility of the atoms (their oscillations increasing). At first only a few atoms, then more and more, get the chance to change neighbours. Finally, the number of these changes per unit of time becomes as great as in liquids.

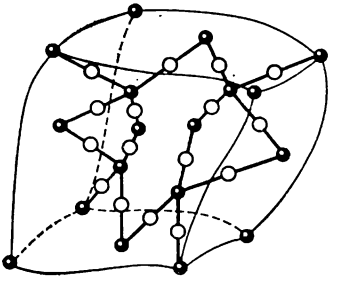


Fig. 77. Structure of amorphous SiO_2

CHAPTER 3

The Gaseous and Other States of Matter

3.1. The Gaseous State

The characteristic feature of the gaseous state is that the molecules (or atoms) of a gas are not held together but freely move about inside a volume that considerably exceeds that of the particles themselves. Intermolecular forces are manifested only when the molecules come sufficiently close to one another. The weak intermolecular interaction determines the low density of gases and their main properties, viz., their tendency to unlimited expansion and capacity to exert pressure on the walls of vessels hindering that tendency.

The state of a gas is characterised by its temperature, pressure, and volume. Its conditions are considered standard or normal at a temperature of 0 °C (273.15 K) and a pressure of 1.01325×10^5 Pa.

Because of the weak intermolecular interaction at low pressures and high temperatures, all typical gases behave approximately

alike, but at normal pressures and temperatures they begin to display their individuality. The essential differences linked with the nature of the particles composing a gas are especially strongly apparent at high pressures and low temperatures, i.e. in the conditions in which they are used in practice in engineering. The raising of external pressure and lowering of temperature brings the particles closer together so that intermolecular interaction becomes more strongly apparent.

In those cases various conditions of equilibrium exist, one of which has the following form (van der Waals' equation)

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where p is the pressure, v the molar volume, T the absolute temperature, R the universal gas constant, and a and b constants of the given gas.

The effect of the forces of attraction acting between the molecules is expressed by the term a/v^2 and the volume proper to the particles by the constant b.

3.2. Plasma

If a substance is heated to temperatures measured in thousands or millions of degrees, it undergoes radical changes and is converted into an ionised gas, or plasma. In the general case plasma is a mixture of continually intermingling atoms, electrons, positive ions, and even atomic nuclei. At temperatures of the order of 10 000 to 100 000 degrees it is called 'cold', and at temperatures of the order of millions of degrees 'hot'. In the latter case neutral atoms can no longer exist in the plasma and it consists of a mixture of electrons, ions, and atomic nuclei. On the whole, plasma is electrically neutral but it possesses electron and ion conductivity.

In terrestrial conditions the plasma state occurs in lightning and the Northern Lights, in electric arcs, in the luminescent material of neon and argon lamps, and in the flames of burners, welding blowpipes and quartz mercury-vapour lamps. The bulk of cosmic matter—stars, nebulae, interstellar matter—also exists as plasma. The Sun is a gigantic cluster of plasma. Cold bodies like Earth are very rare exceptions in the Universe.

The physics and chemistry of plasma are most important and rapidly developing fields of science, not only because plasma is the commonest state of matter in the Universe but also because of the many promising perspectives offered by practical utilisation of the results in these fields. The most hopeful of these prospects are the harnessing of the immense energy of thermonuclear reactions and the mastering of thermochemical synthesis.

3.3. Other States of Matter

Matter also undergoes substantial changes under high external pressures. At pressures of the order of 10^9 to 10^{10} Pa, the distances between atoms in a crystal lattice are reduced and the chemical bonds broken, which creates the conditions for the forming of new bonds corresponding to a denser crystalline structure. Widely known examples of such polymorphous transformations at super-high pressures are the conversion of graphite into diamond, of boron nitride into borazon, and of quartz into a new form (stishovite) with a density 60 per cent higher than that of natural quartz. Polymorphous transformations are beginning to be widely used in industry to synthesise hard and extra-hard substances.

At high and super-high pressures the physical properties of substances are altered. In several cases, substances that are otherwise dielectrics (e.g. sulphur), for instance, become semiconductors at super-high pressures, while semiconductors may be converted to the metallic state at 2×10^{10} to 5×10^{10} Pa. Such transformations have been studied in tellurium, iodine, phosphorus, and certain compounds. It has been calculated that, with a further increase of pressure, all substances can be metallised. Ytterbium (Yb) undergoes interesting transformations: at pressures below 2×10^9 Pa it is a metal; at pressures between 2×10^9 and 4×10^9 Pa it is a semiconductor; while above 4×10^9 Pa it is once again a metal.

Apart from its practical applications, research into the behaviour of substances at such pressures is of great theoretical significance for the development of solid-state physics, geophysics, space physics, and other sciences. Investigations of the properties of terrestrial substance at high pressures and temperatures offers possibilities of simulating processes occurring deep within the Earth and in the Universe, and to study the states of matter in these conditions.

Thus, A. F. Kapustinsky suggests that atoms have a normal electron structure at depths between 60 and 120 kilometres, corresponding to pressures between $2 \cdot 10^4$ and $6 \cdot 10^4$ atmospheres, but that at depths around 3000 km (corresponding approximately to pressures of millions of atmospheres) atoms acquire a quite different structure. Their electron levels would then be filled consecutively to their full capacity, so that the electron structure of cerium, the sixth period element, for example, would be $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{12}$. In those conditions the periodic system would consist of five periods only (containing 2, 8, 18, 32, and 50 elements respectively). The unusual electron structure of atoms would yield a special state of matter, with specific physical and chemical properties. In Kapustinsky's words, this is a zone of 'degenerate chemism'.

The Soviet physicist Lev Landau calculated that conditions are possible in which electrons would be pressed into the atomic nuclei, where they would unite with protons, converting them into neutrons. As a result matter would pass into a *neutron state*. There are grounds for supposing that the transformation of matter into the neutron state may be a stage preceding the spectacular stellar explosion of a supernova. With even greater compression still heavier particles, hyperons, would be generated and matter converted to a new, *hyperonic state*.

These do not, of course, exhaust the states in which matter may exist. The forms of organization of a substance may prove as inexhaustibly rich as the forms of organisation of matter.

Another illustration of the inexhaustibility of the forms of organisation of matter is the concept of *anti-matter*. Present-day data on elementary particles suggest that a special type of matter, or anti-matter, is possible, which would consist of *anti-atoms* formed by *anti-particles*. An anti-atom of anti-hydrogen, for example, would be a system in which the nucleus was an anti-proton (i.e. a proton with a negative charge), around which an anti-electron bearing a positive charge (positron) revolved. There are full grounds for thinking that anti-matter exists in the Universe, forming whole anti-worlds in which anti-matter would be as stable as ordinary matter in our conditions, and capable of existing in various states.

Contact between matter and anti-matter would result in their mutual annihilation and the formation of a field, which may be why anti-matter does not exist in our conditions. Physicists, however, have succeeded in obtaining and studying certain anti-particles. Using high-energy accelerators (30 GeV) they have obtained nuclei of *antideuterium*; in the Serpukhov accelerator (70 GeV), nuclei of *anti-helium*-3 (consisting of two anti-protons and one anti-neutron) (1970) and *antitritium* (1973) have been obtained.

Since enormous energy is liberated during annihilation, a mixture of matter and anti-matter would seem an 'ideal' fuel, of a maximum possible calorific value a thousand times that of fuel employing nuclear fission and thermonuclear processes, and a thousand million times more than the energy of the best modern rocket fuel.

CHAPTER 4

Dispersed Systems

4.1. Solutions

Many substances may be met in several physical states simultaneously, forming a *heterogeneous* system (e.g. water—vapour—ice), but such a system can also be formed by substances of a different nature, i.e. mixtures of various substances in different states.

Heterogeneous systems in which one substance is distributed (dispersed) in another (the medium) in the form of very fine particles are called *dispersed*. The dispersion medium may be gaseous, liquid, or solid. The dispersed substance may also be in various physical states.

Depending on the degree of dispersity (i.e. on the size of the particles distributed in the medium) a dispersed system may be either *coarse* (suspensions and heterogeneous mixtures) with a particle size above one μm, or *finely dispersed* (colloidal), with particle sizes under one μm (1.0-0.1 μm). When a substance is dispersed at the scale of molecules or ions, a *homogeneous* system or *solution* is obtained.

Which type of dispersed system (or solution) is formed depends on the same forces as are responsible for the formation of the state

of aggregation, i.e. on the intensity of the intermolecular, interatomic, interion, or other types of interaction. The difference is solely that the state of aggregation of an individual substance is due to the interaction between its own particles, while the formation of a dispersed system is determined by the character and intensity of the interaction between the particles of different substances.

Dispersed systems are of course far more complicated in structure than the simple states of aggregation of the separate substances and have their own peculiarities.

Solutions are of the greatest importance in chemistry. *A solution is a single-phase system of variable composition consisting of two or more components.* Solutions are homogeneous (uniform) systems, i.e. each component is distributed throughout the other(s) in the form of molecules, atoms, or ions. The component whose physical state does not alter during the formation of a solution is called the *solvent.* When solutions are formed from a mixture of two gases, two liquids, or two solids, the component that predominates in quantity in the solution is taken as the solvent. Solutions may be gaseous, liquid, or solid.

4.2. Gaseous Solutions

Just as in separate substances in the gaseous state, so in a gaseous solution there is also a weak interaction between molecules of the mixed substances. In both cases random motion of the molecules and absence of a definite structure are typical of the system, so that, at normal pressures, a gaseous solution must be considered a physical mixture in which each component retains its specific physical and chemical properties.

An example of a gaseous mixture is air, which consists of nitrogen (78 per cent by volume), oxygen (21 per cent), inert gases (about 1 per cent), carbon dioxide, water vapour, and certain admixtures, all dissolved in one another.

The total pressure exerted by a gaseous mixture is the sum of the pressures (known as *partial pressures*) exerted by its constituents. The total pressure of air, for example, which is 1.01325×10^5 Pa, consists of the partial pressure of nitrogen (78 per cent) $\frac{101\,325 \times 78}{100} = 0.79034 \times 10^5$ Pa, and the partial pressure of oxygen (21 per cent) $\frac{101\,325 \times 21}{100} = 0.21278 \times 10^5$ Pa.

Because of the insignificance of the intermolecular forces operating at ordinary pressures, gases can be dissolved in one another without limit, i e. mixed with one another in any proportion.

At high pressures, particularly when the density of a gas becomes comparable with that of a liquid, the formation of gaseous solutions

is accompanied with changes in volume and with a thermal effect. The mechanism of the dissolution of substances in compressed gases does not differ in principle from that in liquids, and considerable quantities can be dissolved. At 1×10^9 Pa and a temperature of 100 °C, nitrogen, for instance, can dissolve up to 10 moles per cent of benzine, while ethylene, at 2.4×10^7 Pa and 50 °C, can dissolve up to 17 moles per cent of naphthalene. Compressed gaseous solutions are employed in industry to synthesise certain minerals; for example, the solubility of quartz at high temperatures in compressed steam saturated with certain salts is employed to grow large crystals (weighing several kilograms).

4.3. Liquid Solutions

Mendeleev's chemical theory of solutions. Liquid solutions, like individual liquids also have an inner structure of a short-range order, dilute solutions having a structure similar to that of the solvent and concentrated solutions to that of the dissolved substance.

In liquid solutions, the particles of the solute are linked to neighbouring particles of the solvent in complexes known as *solvates* (or *hydrates* in aqueous solutions). This conception of solutions was developed in 1860s by Mendeleev, who suggested, from experimental data, that a solution contained definite chemical compounds of the solute with water. The idea became the foundation of the chemical theory of solutions. The chemical theory of solutions differs in principle from the physical theory, which regarded the solvent as an inert medium and hence treated solutions as simple mechanical mixtures.

Solubility. The solubility of a substance depends on both its nature and that of the solvent.

The structure of liquid benzene, for instance, is governed mainly by the dispersion interaction of nonpolar molecules. If another substance with nonpolar molecules, e.g. hexane, is added to benzene, the character of the molecular interaction will not be altered and the structure of the resultant solution will be determined, as in the separate liquids, by the non-directionality and non-saturability of the dispersion forces, hence the good solubility of hexane in benzene and, conversely, of benzene in hexane. When water is added to benzene, the rupture of the hydrogen bonds (and destruction of the structure of the water) will not be compensated by the formation of new, stronger bonds, which explains the poor solubility of benzene in water.

Alcohol, on the other hand (whose molecules are linked by a hydrogen bond through the OH groups), is readily soluble in water. In this case the rupture of the hydrogen bonds in the water (and

the alcohol) is compensated by the formation of more stable hydrogen bonds between the molecules of water and alcohol.

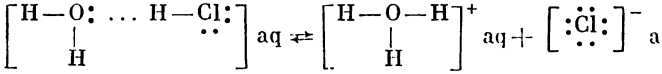
Depending on the nature of the substances involved, the following types of solubility are possible: *unlimited* (water—alcohol, liquid K—Rb, and liquid KCl—KBr), *limited* or *partial* (water—ether, liquid Pb—Zn, liquid LiCl—KCl), practical *insolubility* (water—kerosene, liquid Fe—Ag, and liquid LiF—CsCl). In the last two types separation of the mixed liquids in layers may occur.

Ionisation and dissociation in solution. The interaction of molecules in solutions may be accompanied, as in separate liquids, with their ionisation. The breakdown of a substance into solvated ions under the action of the solvent's molecules is called *ionisation in solution* or *electrolytic dissociation.*

The idea of the ionisation of substances in solutions was first formulated by Arrhenius in 1887. The fathers of the modern theory of electrolytic dissociation as a process induced by the solvation of molecules were I. A. Kablukov and V. A. Kistyakovsky. In contrast to Arrhenius' hypothesis, which did not allow for the interaction of solute and solvent, they explained electrolytic dissociation by Mendeleev's chemical theory of solutions.

The possibility of a solution's breaking up into ions, and the degree to which it does so, depend on the nature of the solute and solvent, and are connected either with *dissociation* (separation) or with *ionisation* (formation of ions). During the dissolution of ionic compounds, for instance, dissociation takes place (since they already consist of ions), the solvents' role being to provide the conditions for separation of ions of opposite sign and to prevent molisation. Ionic compounds dissociate the more readily, the higher the polarity of the solvent's molecules. The breakdown of covalent compounds into ions is connected with heterolytic disruption of the bond, i.e. ionisation.

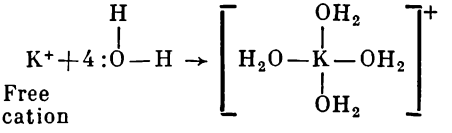
Every substance has a definite *degree of ionisation* in a given solvent and in given conditions. This degree of ionisation is the ratio of the number of ionised molecules to the total number of dissolved molecules. It is determined mainly by the capacity of solvent and solute to donate or accept electrons. For most compounds water, liquid ammonia, and liquid hydrogen fluoride are the most strongly ionising solvents. They have dipole molecules and are susceptible to the donor-acceptor interaction both through unshared electron pairs and by the formation of hydrogen bonds. HCl, for example, is readily ionised in water, owing to the transformation of the hydrogen bond $H_2O \ldots HCl$ into the donor-acceptor bond $[H_2O—H]^+$

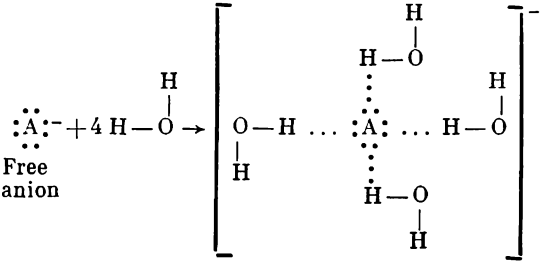


$$H_2O \ldots HCl \rightleftharpoons OH_3^+ + Cl^-$$

For the same reason HCl is readily ionised in alcohol and ammonia. On the contrary, it hardly ionises in nitrobenzene and other solvents that are not susceptible of a donor-acceptor interaction.

Ionic solvates (ionic hydrates). What has been said above shows that complex formation occurs during dissolution, so that solvated complexes are formed (hydrated aquo complexes in aqueous solutions). In cation aquo complexes the central ions are connected with the water molecules through the donor-acceptor interaction, and in anion aquo complexes through hydrogen bonds:





It will be clear that aquo complexes in turn are hydrated, i.e. the water molecules are coordinated around them through hydrogen bonds.

The coordination number of the central ions in aquo complexes in dilute solutions (i.e. in the presence of a considerable quantity of water molecules) generally corresponds to the characteristic coordination number of the cation (acceptor) and the anion (donor). Thus, for Al^{3+}, Cr^{3+}, Co^{2+} the coordination number is usually six, and for Be^{2+} four. In dilute aqueous solution these ions are consequently present in the form of hydrated complex ions of the octahedral $[Al(OH_2)_6]^{3+}$ and tetrahedral $[Be(OH_2)_4]^{2+}$ type. The coordination number of the Cl^- ion, with four unshared electron pairs, is probably four, which corresponds to the formation of four hydrogen bonds.

Aquo complexes are often so strong that they are precipitated from solutions as a part of crystal hydrates like $AlCl_3 \cdot 6H_2O$, $BeCl_2 \cdot 4H_2O$, etc.

The coordination sphere of ions is not, as a rule, indicated in equations and a simplified form is used in practice:

$$AlCl_3\ (sol) \rightleftarrows Al^{3+}\ (sol) + 3Cl^-\ (sol)$$

$$BeSO_4\ (sol) \rightleftarrows Be^{2+}\ (sol) + SO_4^{2-}\ (sol)$$

Energy effect of solution. During dissolution, the bonds between the molecules (atoms or ions) in both the solvent and the solute are broken and this involves an expenditure of energy. At the same time, complexes are formed (solvation), i.e. bonds are formed between the particles of the solute and the solvent, which is accompanied with a release of energy. The overall energy effect depends on the ratio between the energy liberated and absorbed and may be either positive or negative. When gases and liquids are dissolved heat is evolved as a rule, particularly when water and alcohol are mixed. When solids are dissolved in water heat may either be liberated, as with $Ca(OH)_2$ and KOH, for example, or be absorbed, as with NH_4NO_3. Raising of the temperature therefore affects solubility in different ways. If the dissolving of a substance is accompanied with a liberation of heat, its solubility falls when it is heated, for example KOH and $Ca(OH)_2$. But if a substance dissolves with absorption of heat, heating will enhance its solubility (NH_4NO_3). The solubility of gases usually falls with rising temperature but increases as pressure is raised.

Duality of liquid solutions. The energy effect apart dissolution is also accompanied with changes in volume. When alcohol is dissolved in water, for example, the total volume of the solution is about 3.5 per cent less than would be expected from adding together the volumes involved, because of the formation of solvates.

The colour of substances also often changes in solution. White copper sulphate $CuSO_4$ forms a blue aqueous solution through the formation of hydrated aquo complexes $[Cu(OH_2)_6]^{2+}$.

All these facts (energy effect of solution, and changes in volume and colour) indicate that liquid solutions need to be regarded as chemical compounds. The absence of constant composition in solutions, however, i.e. the absence of a definite ratio between the quantities of solute and solvent, approximates them to mechanical mixtures. So liquid solutions occupy an intermediate position between chemical compounds of definite composition and mechanical mixtures.

According to Mendeleev, the formation of solutions can be considered from two aspects, the chemical and the physical, and solutions show, more clearly than anything else, how close these aspects of natural science are to each other.

As in individual liquids, thermal motion in liquid solutions consists mainly in oscillations about temporary points of equilibrium in complexes and abrupt migrations from one complex to

a neighbouring one. These jumps make liquid solutions resemble gaseous solutions, i.e. physical mixtures, and cause diffusion by which a uniform concentration of the solute is maintained throughout the solution. As a rule, a solute spreads almost as easily in a liquid solution as in a gas. The constant motion of the particles also determines such properties of liquid solutions as viscosity, fluidity, thermal conductivity, electrical conductivity, etc.

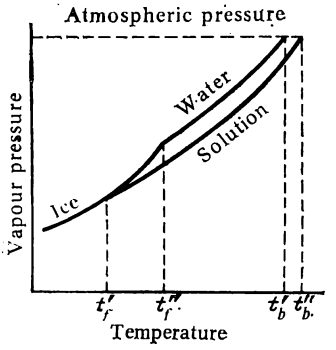


Fig. 78. Vapour pressure of water and a solution

Boiling and freezing points of solutions. When a nonvolatile substance is added to a solvent, vapour pressure above the solution falls, which raises its boiling point and lowers its freezing point (compared with the pure solvent).

Let us consider the variation of vapour pressure with temperature for pure water and for an aqueous solution of a nonvolatile substance. The curve of the dependence of the solution's vapour pressure on temperature (as can be seen from Fig. 78) lies below the curve for pure water. Under normal pressure pure water boils at 100 °C (373.15 K) since its vapour pressure at this temperature is equal to the external pressure. For a solution to boil, the vapour pressure of the solvent must be equal to that of the atmosphere, which happens when its temperature t''_b is higher than that of the pure solvent t'_b.

A liquid freezes (solidifies) when its vapour pressure equals that of the corresponding solid phase. Figure 78 shows that the vapour pressure of ice is attained in a solution at a temperature t'_f lower than that of pure water t''_f. The lowering of the freezing point of solutions was first established by Lomonosov in 1748.

Research into the properties of dilute solutions of nonelectrolytes has shown that the degree to which vapour pressure is lowered, and the boiling point elevation and freezing point depression, depends simply on the number of dissolved particles in a certain volume of the solvent, and not on the properties of the solute (which is the essence of *Raoult's law*).

The dependence of the freezing point depression Δt_f and of the boiling point elevation Δt_b on the concentration of a nonelectrolyte in dilute solutions can be expressed in general form as follows:

$$\Delta t_f = k_f c \quad \text{and} \quad \Delta t_b = k_b c$$

where k_f and k_b are the *cryoscopic* and *ebullioscopic* constants respectively which depend on the nature of the solvent; c is the concentration of the solute (number of moles per 1000 grams of the solvent).

Values of the constants for selected solvents are given below:

	k_f	k_b
Water	1.86	0.52
Benzene	5.10	2.64
Acetic acid	3.90	3.10

Concentration can be replaced by the ratio of the mass of the solute m per 1000 g of the solvent and its molecular weight M. Then

$$\Delta t = k \frac{m}{M}$$

This formula simplifies calculation of the molecular weight of the substance.

The depression of the freezing point and elevation of the boiling point of solutions of electrolytes are always greater than theoretically calculated. The freezing point of a solution containing one mole of NaCl per 1000 g of water, for example, is lowered by 3.36 °C, i.e. almost twice as much as in similar solutions of nonelectrolytes. The fact is explained at present by the increased number of solvated particles produced by ionisation of the electrolyte. The various attempts to explain this phenomenon in his day enabled Arrhenius to suggest an hypothesis of ionisation that has become one of the most important theories in modern chemistry.

Acids and Bases. As we have already seen, the ionisation of compounds of hydrogen with a +1 oxidation state in the liquid state gives rise to positive and negative solvated ions:

$$H_2O \ldots H_2O \rightleftharpoons OH_3^+ + OH^-$$
$$H_3N \ldots H_3N \rightleftharpoons NH_4^+ + NH_2^-$$

The dissolving of one and the same compound in corresponding media raises either their donor (basic) function or their acceptor (acidic) one. When HCl or HNO_3, for example, is dissolved in water, hydrated oxonium ions and corresponding anions are formed:

$$H_2O \ldots HCl \rightleftharpoons OH_3^+ + Cl^-$$
$$H_2O \ldots HNO_3 \rightleftharpoons OH_3^+ + NO_3^-$$
Donor Acceptor

Dissolution of these same substances in liquid ammonia is accompanied with the formation of solvated ammonium ions and the corresponding anions:

$$H_3N \ldots HCl \rightleftharpoons NH_4^+ + Cl^-$$
$$H_3N \ldots HNO_3 \rightleftharpoons NH_4^+ + NO_3^-$$
Donor Acceptor

As will be seen from these examples, the HCl and HNO_3 molecules act as acceptors of electron pairs through proton transfer, i.e. they are acidic compounds. At the same time, the molecules

of the solvent (water or ammonia), by gaining protons, act as donors of electron pairs, i.e. behave like basic compounds. As a result of the donor-acceptor interaction the concentration of positive ions (OH_3^+ in water and NH_4^+ in liquid ammonia) increases compared with the pure solvent. What has been said enables us to formulate the following partial definition of acids: *an acid is a compound which, when dissolved, increases the concentration of the solvent's positive ions.*

The concentration of positive ions may also be increased through the dissolution of compounds containing *onium* radicals, viz. oxonium derivatives in aqueous media (e.g. OH_3Cl, OH_3NO_3), ammonium derivatives in liquid ammonia (e.g. NH_4Cl, NH_4NO_3), etc. The higher concentration of the positive ions is here not the result of an acid-base interaction, but is linked with simple dissociation.

HCl and HNO_3 can also act as basic compounds when dissolved in appropriate solvents. In liquid hydrogen fluoride, for example, the HCl and HNO_3 molecules unite with a proton from the HF molecules, so acting as donors of electron pairs, while the HF molecules, for the same reason, are acceptors of electron pairs. As a result of the donor-acceptor interaction, the concentration of F^- ions (the negative ions of the solvent) is higher than in pure hydrogen fluoride:

$$\begin{array}{c} HNO_3 \ldots HF \rightleftharpoons NO_3H_2^+ + F^- \\ HCl \ldots HF \rightleftharpoons ClH_2^+ + F^- \\ \text{Donor} \quad \text{Acceptor} \end{array}$$

The number of the OH^- ions (negative ions of the solvent) in aqueous solutions is increased, for example, when ammonia is dissolved in water:

$$\begin{array}{c} H_3N \ldots HOH \rightleftharpoons NH_4^+ + OH^- \\ \text{Donor} \quad \text{Acceptor} \end{array}$$

From the idea developed above, we get the following definition of a base: *a base is a compound which, when dissolved, increases the solvent's concentration of negative ions.*

The concentration of negative ions of the solvent can also be increased by dissolving certain compounds in it that contain appropriate radicals. The most easily dissociated of such compounds are alkalis, which are hydroxides in aqueous solutions, e.g. KOH and $Ba(OH)_2$, and dihydronitrides in liquid ammonia, e.g. KNH_2 and $Ba(NH_2)_2$.

When acids and bases react with one another, molecules of the solvent are liberated, i.e. a neutralisation reaction occurs: as for example,

in water: $KOH + OH_3Cl = KCl + 2H_2O$

in liquid H_3N: $KNH_2 + NH_4Cl = KCl + 2H_3N$

The degree and character of acid-base ionisation in a system of two compounds of hydrogen(I) depend on their donor-acceptor capacity. Thus, in the series $HF—H_2O—H_3N$, proton affinity increases as the number of unshared electron pairs declines. Since proton affinity is greater in H_3N (9.3 eV) than in H_2O (7.9 eV) acids that are weak in aqueous solutions are ionised much more strongly in liquid ammonia. HCN, for example, is a very weak acid in water but in ammonia it is ionised almost as strongly as HNO_3 in water. Even certain hydrocarbons display acid properties in liquid ammonia. And water, when dissolved in HF, acts as a base.

4.4. Solid Solutions

Just as in individual crystalline substances, the atoms, ions, and molecules in solid solutions are held in a crystal lattice by interatomic. interionic, and intermolecular forces, but the lattice of a solid solution is formed by particles of two or more substances randomly distributed relative to one another. In other words, a solid solution is a mixed crystal. Depending on the arrangement of particles, solid solutions may be either *substitutional* or *interstitial.*

Substitutional solutions are formed when the lattices of the components are of the same type and their particles of similar size. A *sine qua non* of the formation of solid solutions is also a certain similarity of the substances' chemical properties (e.g. an identical type of chemical bonds). In a crystal of KCl, for instance, the chloride ions can be gradually replaced by bromide ions, i.e. there can be practically continuous transfer of matter between KCl and KBr without noticeable change in the stability of the crystal lattice. The properties of the solid solutions formed change continuously from those of KCl to those of KBr. Examples of ionic, atomic, molecular, and metallic substitutional solid solutions are given below:

Crystal lattice	*Continuous series of substitutional solid solutions*
Covalent	Si—Ge, Se—Te
Ionic	KCl—KBr, $K_2SO_4—K_2BeF_4$
Metallic	Ag—Au, Au—Pt
Molecular	$Br_2—I_2$

If the particles of one component are less than two-thirds the size of those of the other, an interstitial solid solution may be formed through the smaller particles penetrating to the interstices of the lattice formed by the larger particles. Interstitial solutions are formed, for example, with joint crystallisation of iron and carbon, during the adsorption of hydrogen on certain metals, and so on.

The formation of solid solutions is accompanied (as with liquid solutions) with a thermal effect, changes in total volume, and changes in some of the components' original properties.

Solid solutions are generally obtained through the crystallisation of liquid solutions. A solid Ag—Au solution forms through crystallisation of their liquid alloy. Mixed KCl—KBr crystals are produced during joint crystallisation from an aqueous solution or a melt, and so on.

4.5. Eutectic Mixtures

Substances that are poorly soluble in each other in the solid state often form what is called a *eutectic* mixture when crystallised from their melts (within certain ratios of concentration). A eutectic mixture (Gr. *eutektos* easily melting) has a melting point lower than those of its components. The melting points of Bi and Cd, for example, are 271 °C and 321 °C respectively, but their alloy, containing 40 per cent Cd and 60 per cent Bi, melts at 144 °C. A solution containing NaCl (23.4 per cent) and H_2O (76.6 per cent) crystallises at —21.2 °C. A eutectic mixture of LiCl and KCl melts at 350 °C though the melting points of LiCl and KCl are 614 °C and 776 °C respectively.

CHAPTER 5

Physicochemical Analysis

5.1. Thermal Analysis

Physicochemical analysis is based on the study of the dependence of a system's physical properties on its composition or external conditions, which enables us to discover and study the chemical changes taking place within it. Physicochemical analysis was first suggested as a method of research by Lomonosov. Mendeleev used it to study densities of solutions. A major theoretical and experimental contribution to the fundamentals of physicochemical analysis, converting it into an independent discipline, was made by N. S. Kurnakov.

The chemical transformations in a system can be judged, for example, from the character of the changes in its various physical properties (e.g. melting and crystallisation points, vapour pressure, viscosity, density, hardness, magnetic properties, and electrical conductivity), produced by changes in its composition. The results of the investigations are usually presented in the form of a composition-property diagram, in which the composition of the system is plotted along the x-coordinate and its properties along the y-coordinate.

The most commonly used method of physicochemical analysis is thermal analysis. During the investigation, a *phase* or *constitutional diagram*, which expresses the dependence of the system's melting point on its composition, is constructed and studied.

The diagram is constructed as follows. Two pure substances are mixed in various proportions. Each mixture is then melted and cooled gradually. The temperature of the melt is taken at regular intervals during cooling and recorded, and a cooling curve plotted. Figure 79 shows the cooling curves for a pure substance (*1*) and an alloy (*2*). The transition of the pure substance from the liquid to the solid state is accompanied with liberation of latent heat of crystallisation. Therefore, the temperature remains constant until all the liquid is crystallised. A solid's further cooling proceeds uniformly.

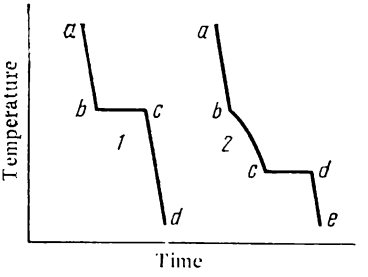


Fig. 79. Curves of the cooling of (*1*) a pure substance and (*2*) a mixture of two substances forming a eutectic

When a melt (solution) is cooled, the cooling curve has a more complicated form (Fig. 79, curve *2*). In the simplest case of the cooling of a melt of two substances, the temperature at first falls uniformly until crystals of one of them begin to be precipitated. As solutions crystallise at lower temperatures than pure solvents, the temperature at which one of the components begins to separate out from the solution is higher than the latter's crystallisation point. As crystals of one of the components are precipitated, the composition of the liquid solution is altered and its freezing point falls continuously as crystallisation proceeds. The heat liberated during crystallisation slightly retards cooling, so that from point *b* the slope of the curve is not so steep as before. Finally, when the melt becomes saturated as regards both substances (point *c*), both begin to crystallise simultaneously. This corresponds to the horizontal portion of the curve (*cd*). When crystallisation is finished there is a further drop in temperature.

The data obtained with mixtures of various composition are used to construct a phase diagram.

5.2. Types of Phase Diagram

The most typical phase diagrams are shown in Figs. 80 to 84.

A system with a eutectic mixture. A phase diagram for substances that are indefinitely soluble in one another in the liquid state but insoluble in the solid state is shown in Fig. 80. When a melt of

zinc and tin is cooled slowly, either zinc or tin will crystallise first. During the cooling of a 60/40 solution of zinc and tin, for example, the zinc begins to separate out first in the solid phase, which happens when its temperature of solidification from a melt of this composition is reached (point *a*). Since solutions crystallise at lower temperatures than pure liquids (Fig. 78), the temperature at which zinc begins to separate out from the melt is lower than its freezing point (419 °C). As the zinc separates out, and the system

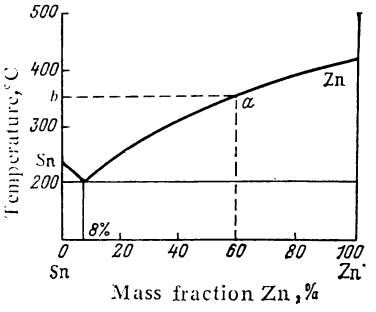


Fig. 80. Phase diagram of a system with a eutectic

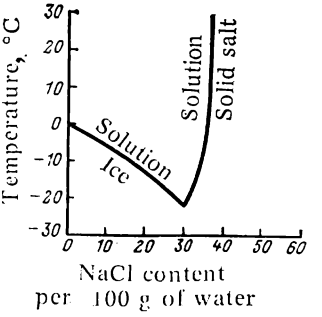


Fig. 81. Phase diagram of an H_2O—NaCl system

becomes richer in tin, the crystallisation point of solution falls even further, and at the eutectic point (92 per cent Sn and 8 per cent Zn) the solution crystallises as a whole. When a melt containing 92 per cent Sn and 8 per cent Zn is cooled, the composition of the solid phase is a pure eutectic mixture. With other proportions of the components in the melt, a mixture of the eutectic and of larger crystals of zinc or tin, that separated out earlier, is formed.

Systems of salts (LiCl—KCl), of a simple substance and a compound (Cu—CuO, Ni—NiS), and of water and a salt, etc., have a similar phase diagram.

The phase diagram of the crystallisation of a salt from its aqueous solution is shown in Fig. 81. The eutectic mixture in a water/salt system is called a *cryohydrate*. In the H_2O—NaCl system (Fig. 81) this corresponds to 23.4 per cent of NaCl; the crystallisation point is —21.2 °C. Since ice melts at 0 °C, any cryohydrate mixture will melt at a temperature below 0 °C. Cryohydrates are used to obtain low temperatures.

A system of substances forming a chemical compound. When a chemical compound is formed during the melting of a substance, this is reflected in the phase diagram by the appearance of a maxi-

mum corresponding to the composition of the compound (Fig. 82*a*). In the system Mg—Sb, for example, the maximum corresponds

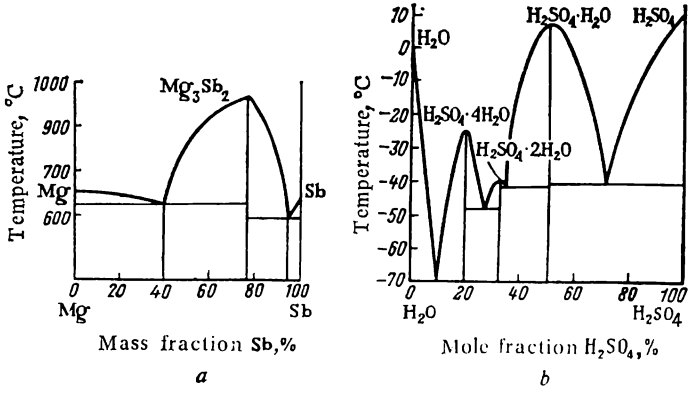


Fig. 82. Phase diagram of a system with a new compound:
a—Mg—Sb system; *b*—H_2O—H_2SO_4 system

to the melting point of the compound Mg_3Sb_2. This phase diagram is a kind of combination of those of Mg—Mg_3Sb_2 and Mg_3Sb_2—Sb systems.

If a phase diagram has several peaks, this indicates that the system contains several compounds. From the peaks on the phase

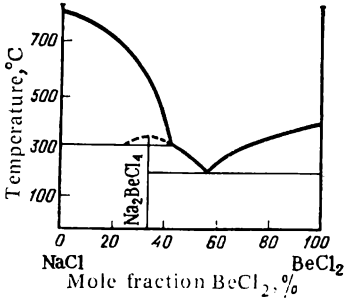


Fig. 83. Phase diagram of a system with an unstable compound

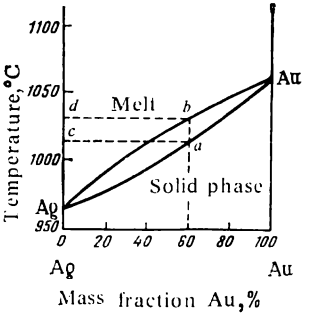


Fig. 84. Phase diagram of a solid solution

diagram of an H_2O—H_2SO_4 system we can conclude that the following compounds exist in it: H_2SO_4, $H_2SO_4 \cdot H_2O$, $H_2SO_4 \cdot 2H_2O$, and $H_2SO_4 \cdot 4H_2O$ (Fig. 82*b*).

If an unstable compound that decomposes completely before the melting point is reached is formed in a system, the phase diagram has the form shown in Fig. 83. The point at which the curve breaks corresponds to the temperature of decomposition of this compound:

its composition can be established by extending the lower portion of the curve to its maximum. The curves describing an $NaCl—BeCl_2$ system, for example, show that an unstable compound corresponding to an Na_2BeCl_4 composition is formed.

A system of substances forming solid solutions. A typical feature of such systems is that the melting point of a solid solution of a given composition does not coincide with the solidification point of a liquid solution (melt) of the same composition. Two curves can therefore be seen in Fig. 84, the upper one giving the solidification points of the melt and the lower one the melting points of the solid solution. The moment at which a solid solution containing 60 per cent of gold begins to melt corresponds to point *c* on the diagram and the moment at which a melt of the same composition begins to solidify corresponds to point *d*.

The three main types of phase diagram described correspond to the simplest cases. In practice, however, we usually get diagrams of a more complicated form combining signs characteristic of the simplest separate diagrams.

Thermal analysis is especially important for studying metal alloys.

IV

METHODS OF INVESTIGATING THE STRUCTURE OF SUBSTANCES

> It was necessary first to examine things before it was possible to examine processes. One had first to know what a particular thing was before one could observe the changes it was undergoing.
>
> Frederick Engels. *Ludwig Feuerbach and the End of Classical German Philosophy*

We get information about the structure of matter by studying its physical and chemical properties. Study of absorption and emission spectra, the diffraction of radiation of various kinds, magnetic and electrical interactions, and the mechanical, thermal, electrical, and other characteristics of substances, has a special role in this.

We draw our final conclusion about the properties of a particular substance after comparing and cross-checking the information obtained by various methods.

CHAPTER 1

Spectroscopic Methods

1.1. The Electromagnetic Spectrum and Atomic or Molecular Processes

The spectra of the electromagnetic radiation emitted, absorbed, or diffused by matter are studied by the branch of physics known as *spectroscopy*. A quantum of absorbed or emitted energy corresponds to an alteration of energy because of some single atomic act or molecular process (see Table 11). The shortest radiation (gamma-radiation) corresponds to nuclear processes. The quantum transitions of the inner electrons of atoms and molecules are accompanied with X-rays. Electromagnetic radiation in the ultraviolet and visible regions of the spectrum corresponds to quantum transitions of the outer electrons. Infrared radiation corresponds to the oscillation of atoms in molecules, far infrared radiation to the rotation of molecules; radio-frequency radiation corresponds to the spin transition of electrons and nuclei.

The following types of spectroscopy are distinguished according to the range of wavelengths of the electromagnetic radiation concerned: *gamma-spectroscopy*, *X-ray spectroscopy*, *optical spectroscopy*, and *radiospectroscopy*. Optical spectroscopy in turn is divided into visual, infrared, and ultraviolet spectroscopy.

Table 11. **Atomic and Molecular Processes and Electromagnetic Spectra** *

Process	Spectral region of radiation	Wavelength λ, cm	Wave number $\tilde{\nu} = 1/\lambda$, cm^{-1}	Radiation energy quanta, $\Delta E = h\nu$, eV
Nuclear reactions	Gamma-radiation	10^{-10}	10^{10}	1.24×10^6
Electron transitions:				
inner electrons	X-rays	10^{-9}-10^{-7}	10^9-10^7	1.24×10^5-1.24×10^3
outer electrons	Ultraviolet radiation and visible light	10^{-6}-10^{-4}	10^6-10^4	124-1.24
Atom oscillations in molecules	Near infrared radiation	10^{-3}	10^3	0.124
Molecule rotation	Far infrared radiation	10^{-2}	10^2	0.0124
Spin transitions:				
of electrons	Radiofrequency radiation	10^{-1}-10^2	10-10^{-2}	1.24×10^{-3}
of nuclei		10^3-10^5	10^{-3}-10^{-5}	1.24×10^{-9}

* Electromagnetic radiation can be characterised by either wave or energy parameters. The former are wavelength λ, oscillation frequency ν, and wave number $\tilde{\nu}$. The wave number indicates the number of waves of a given wavelength per centimetre; it is measured in cm^{-1}.

1.2. X-ray Spectroscopy

X-rays are generated through quantum transitions of the inner electrons of atoms, which becomes possible as a result of irradiation of matter by a beam of high energy electrons or hard X-rays by which electrons are knocked out of the inner electron levels of the atom shells. The orbitals freed are then filled with electrons from levels further away from the nucleus (Fig. 85), which is accompanied with the emission of quanta of X-rays.

Since the electron quantum transitions in atoms of various elements differ in energy, X-rays depend on the atom's structure. This

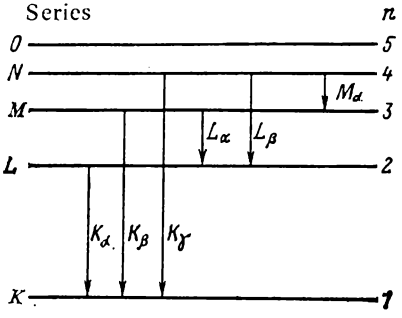


Fig. 85. Diagram of the rise of X-ray spectra (n = the principal quantum number)

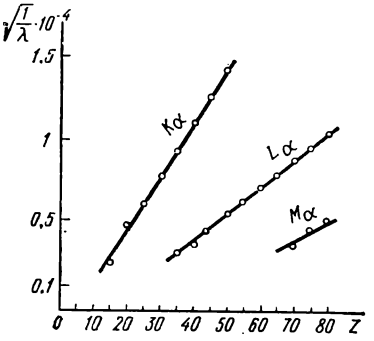


Fig. 86. Dependence of the wavelength of X-rays on atomic number

dependence is described by Moseley's law (Fig. 86) that the wavelengths of X-rays of atoms are proportional to the atomic numbers of the elements

$$\sqrt{1/\lambda} = a\,(Z - b)$$

where λ is the wavelength; Z is the atomic number of the element; and a and b are constants identical for similar lines in a given series of X-rays (e.g. K_α, L_α, M_α).

Moseley's discovery of this dependence (1913) played an important role in clarifying atomic structure (confirming, in particular, the atom's shell structure), enabled the atomic number of an element to be determined experimentally, and confirmed the arrangement of the elements in Mendeleev's periodic system. It also enabled the X-ray spectra of hafnium, rhenium, and other elements not then known, but subsequently discovered, to be calculated.

To obtain X-ray spectra (see Fig. 87), a beam of electrons *3* is focussed from a cathode *1* onto the anticathode *2* of an X-ray tube. The anticathode is made

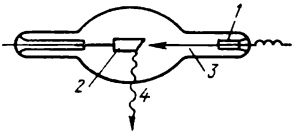


Fig. 87. Diagram of an X-ray tube

either of the simple substance whose spectrum is to be investigated or of platinum coated with a compound of the element concerned. The X-rays *4* generated at the anticathode are directed through a crystal (which acts as a diffraction

grating) onto a photographic plate. When the plate is developed, the lines of the spectrum become apparent. X-ray spectra are now generally obtained by exciting substances with hard X-rays.

X-ray analysis is used for quantitative (from the intensity of the spectral lines) and qualitative determination of the elements in materials of complex composition.

X-ray spectrum analysis enables the effective charges on atoms to be determined and hence the type of chemical bond in compounds. For this the lines of the X-ray spectrum of free atoms are compared with those of their compounds. When an atom in a compound has a corresponding effective charge δ, the spectral lines are shifted compared with the spectrum of the free atom. The value of δ can be determined from the magnitude of this shift by the appropriate calculations. The values of the effective charges of the atoms in certain compounds, calculated in this way, are given in Table 12.

Table 12. **Effective Charges δ of Atoms of Selected Compounds**

Compound	Atom and its oxidation state	Effective charge δ	Compound	Atom and its oxidation state	Effective charge δ
HCl	H(I)	+0.18	$CrCl_2$	Cr(II)	+1.9
NaF	Na(I)	+0.58	$CrCl_3$	Cr(III)	+1.2
NaCl	Na(I)	+0.92	$[Cr(NH_3)_6]Cl_3$	Cr(III)	+1.2
NaBr	Na(I)	+0.83	K_2CrO_4	Cr(VI)	+0.2
NaI	Na(I)	+0.75	$K_2Cr_2O_7$	Cr(VI)	+0.1
$MgCl_2$	Mg(II)	+1.5	$KMnO_4$	Mn(VII)	+0.3
$MgBr_2$	Mg(II)	+1.38	$CaSO_4$	S(VI)	+0.4
MgO	Mg(II)	+1.01	$KClO_3$	Cl(V)	+0.7
MgS	Mg(II)	+1.05	$K_3[Fe(CN)_6]$	Fe(III)	+1.0
SiO_2	Si(IV)	+1.97	OsO_2	Os(IV)	+0.8
SiS_2	Si(IV)	+1.69	$K_2[OsO_4]$	Os(VI)	+0.8
$Co(NO_3)_2$	Co(II)	+1.2	$K[OsO_3N]$	Os(VIII)	+1.0

The values of effective charges obtained by various methods differ. But the values of δ available indicate that the atoms in compounds do not carry high charges and there are no purely ionic compounds.

1.3. Optical Spectroscopy

The spectra of molecules are far more complicated than those of atoms. Molecular spectra are made up of bands (Fig. 88) rather than of separate lines (see Fig. 6). Their complexity depends on the fact that, in addition to the electron's motion relative to the nuclei

in a molecule the latter themselves also vibrate, while the molecules as a whole rotate. For each of these types of motion (or quantum

Fig. 88. Emission spectrum of nitrogen molecules in the near ultraviolet region

transitions) there is a corresponding spectrum, viz., electronic, vibrational, and rotational (see Table 11).

The energy of electron transitions is the highest (1-100 eV). The changes in them are reflected in the ultraviolet and visible regions of the spectrum. The energy of vibrational transitions (10^{-1} to 10^{-2} eV) corresponds to emission (absorption) in the near infrared region. The rotational transitions of molecules have the lowest energies (10^{-3} to 10^{-5} eV), which correspond to emission or absorption in the far infrared region, or even in that of radio frequencies (see Table 11).

When a molecule is excited, complicated energy changes occur in it (Fig. 89): electrons move from one level to another, and the system of possible oscillatory and rotational levels is altered at the same time. This complicates the spectrum and forms a characteristic line structure that distinguishes molecular spectra sharply from the line spectra of atoms.

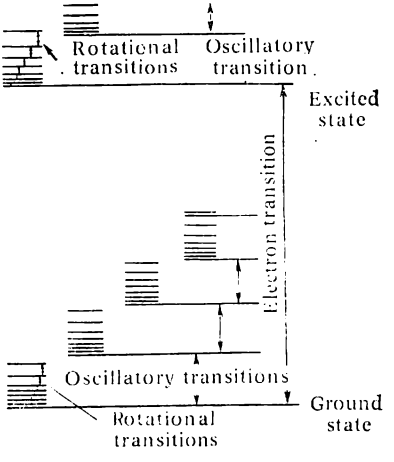


Fig. 89. Diagram of the electron, oscillatory, and rotational levels of a diatomic molecule

When molecular absorption spectra are studied (Fig. 90), a beam of light is directed into a monochromator *2* (a prism or a diffraction

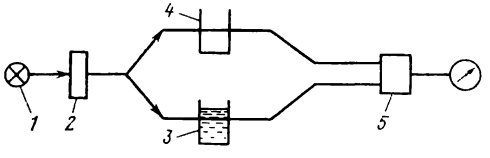


Fig. 90. Diagram of spectroscope

grating) where it is decomposed into a spectrum. Parallel beams of monochromatic light of the appropriate wavelengths are then

passed through a cell *4* (either empty or filled with a solvent) and through a cell *3* filled with the test substance (or with a solution of this substance in the same solvent as in cell *4*). Both beams are directed onto a photosensitive device *5*, where their intensities are compared. The procedure is repeated for various new wavelengths

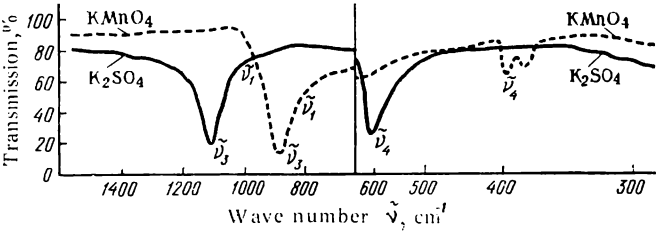


Fig. 91. Infra-red spectra of K_2SO_4 and $KMnO_4$

through the entire measuring range. Modern instruments by means of radio engineering diagrams automatically record the absorption spectra in the form of absorption curves (Fig. 91), on which the amount of absorbed light of a given energy (absorbed intensity) is plotted along the y-axis and the energy of the quanta, expressed in wavelengths, oscillation frequency, or wave number, along the x-axis.

Visible and ultraviolet spectroscopy. Electronic transitions are studied by means of visible or ultraviolet light, which allows the

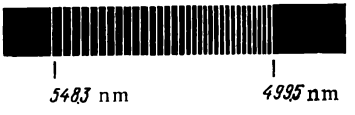


Fig. 92. Absorption spectrum of iodine vapour

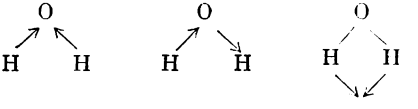
energy of a molecule's orbitals, its ionisation energy, and the energy of the chemical bond to be determined. The last-named is determined from the effect of radiation that causes dissociation of molecules. The absorption spectrum of iodine vapour is shown in Fig. 92. At wavelength of 499.5 nm the band spectrum changes into a continuous one corresponding to dissociation of the iodine molecule. Knowing the wavelength λ at which dissociation occurs, we can easily calculate the bond dissociation energy and hence the bond energy. Selected bonding energies are given in Table 13.

Table 13. **Energy of Selected Interatomic Bonds**

Bond	Bond energy, kJ/mol	Bond	Bond energy, kJ/mol	Bond	Bond energy, kJ/mol
Li—Li	99.0	Br—Br	199.0	H—Br	363.5
Na—Na	71.1	I—I	150.7	H—OH	498.7
K—K	53.6	N≡N	940.3	O—H	427.8
H—H	435.1	H—F	565.7	C—H	415
F—F	159	H—Cl	431.6	Hg—Hg	7.5
Cl—Cl	242.2				

Infrared spectroscopy. Infrared radiation is used to study the vibrational spectrum of molecules. The frequency of the vibration is generally determined by the mass of the oscillating atoms and groups of same and the rigidity of the chemical bond. The latter is characterised by the *force constant k* expressed in N/m.

Atoms can vibrate either along the line of the chemical bond (stretching vibrations) or through changes in their valence angles (bending vibrations) as becomes apparent in the example of the water molecule:



$\tilde{\nu} = 3657\ cm^{-1}$ $\tilde{\nu} = 3756\ cm^{-1}$ $\tilde{\nu} = 1595\ cm^{-1}$

Force constants can be calculated from the wave number of stretching vibrations; they depend on the nature of the bonded atoms and multiplicity of the bond (see Table 14).

Table 14. **Wave Numbers and Force Constants of Stretching Vibrations of Selected Molecules**

Molecule	Wave number, $\tilde{\nu}$, cm^{-1}	Force constant, *k*, N/m	Molecule	Wave number, $\tilde{\nu}$, cm^{-1}	Force constant, *k*, N/m
H_2	4395.2	573.4	F_2	892	718.6
D_2	3118.4	576.8	Cl_2	564.9	328.6
HF	4138.5	965.5	I_2	214.6	172.1
HCl	2989.7	515.7	O_2	1580.4	1177
HBr	2649.7	411.8	N_2	2359.6	2296
HI	2309.5	314.1	CO	2170.2	1902

As will be seen from the table the force constants of molecules with multiple bonds (N_2, CO, O_2) are much higher than those of molecules with single bonds.

The presence in the infrared spectrum of an unknown substance of lines characteristic of certain groupings of atoms (C=O, O—H) enables its composition and structure to be suggested.

The energy of rotational transitions depends on the mass and configuration of a molecule. Hence the study of rotational spectra (long-wave infrared and radio frequencies) provides information about the spatial structure of molecules, internuclear distances, and valence angles.

1.4. Radiospectroscopy

The most important radiospectroscopic methods are *nuclear magnetic resonance* (NMR) and *electron spin resonance* (ESR) or *electron paramagnetic resonance* (EPR), which are based on the fact that magnetic energy levels are induced in the nuclei (NMR) and electrons (ESR) of a substance placed in a strong magnetic field. These induced levels correspond to changes in the spin of the nucleus or the electron, the spin energy transitions corresponding to the absorption of quanta of radio waves.

In experiments with nuclear magnetic resonance (Fig. 93) the test substance *1* is placed in a resonator located between the poles of an electromagnet. Radio signals are passed through the resonator and their intensity recorded by an instrument *3*. The frequency of the radio waves is kept constant during the test, while field intensity is gradually increased.

At a certain intensity of the magnetic field, conditions for spin transition of the nuclei are created, a moment corresponding to the absorption of radio wave energy by the substance, which is also recorded.

The results of the investigation are recorded as a NMR absorption curve (Fig. 94) which expresses the dependence of the energy absorbed

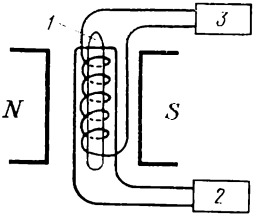


Fig. 93. Diagram of a NMR spectroscope:
1—ampoule with sample; *2*—radio-frequency generator; *3*—detector

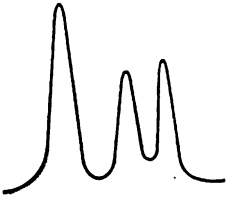


Fig. 94. NMR (proton) absorption curve of ethyl alcohol

on the intensity of the magnetic field. The spin transitions of a nucleus depend on the state of the atom's electron shell. Different molecules and the different groups of atoms in them therefore absorb

at different intensities of the magnetic field. Analysis of the shapes and position of the peaks on the curve enables conclusions to be drawn about the properties and structure of the compounds. Analysis of the NMR absorption curve for ethyl alcohol, for example, shows that the peaks (Fig. 94) correspond to the spin transitions of the protons of the atom groupings CH_3, CH_2, and OH. The structure of the C_2H_5OH molecule is confirmed in this way.

The EPR (or ESR) method employs the resonance absorption of radio waves by electrons. It is used to study paramagnetic substances, i.e. those having unpaired electrons, and is widely employed

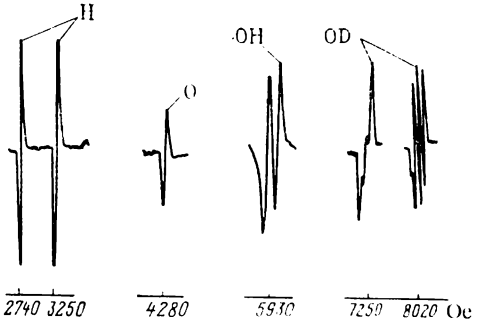


Fig. 95. ESR spectra of H and O atoms and free OH and OD radicals

to detect and determine the concentration of free radicals and ions in solutions, establish the character of the chemical bonds in complex compounds, and so on.

The EPR method is employed to study the mechanism of chemical reactions. When the reactions between hydrogen and oxygen are studied, for example, the spectra shown in Fig. 95 are observed, which confirm that the reaction between H_2 and O_2 has a chain mechanism and proceeds through the formation of free radicals. When H_2 is replaced by D_2 peaks characteristic of deuterium atoms and OD radicals appear in the spectrum.

The phenomenon of paramagnetic resonance was discovered by E. K. Zavoisky in Kazan in 1944. Nuclear magnetic resonance was discovered by the American physicists E. Purcell and F. Bloch (1946).

1.5. Gamma-ray Spectroscopy

Gamma-ray spectroscopy is based on the resonance absorption of gamma-quanta by atomic nuclei (*Mössbauer effect*). As the nuclei undergo radioactive decay, isotopes in an excited state are formed.

Their transition to the ground state is accompanied with gamma-radiation. Unexcited atomic nuclei in turn can absorb gamma-quanta and so be excited, but only in special conditions. The gamma-emission of excited ^{57}Fe nuclei of a metal plate can absorb the unexcited nuclei of ^{57}Fe of another plate. If the source and the acceptor

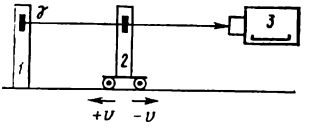


Fig. 96. Diagram of apparatus for studying the absorption of gamma-radiation

of gamma-rays are in different compounds (e.g. the source of ^{57}Fe in metal and the absorber in a crystal of $FeCl_2$) gamma-rays will not be absorbed.

This is explained by the energy of nuclear transitions depending on the distribution of electron density around the nucleus, i.e.

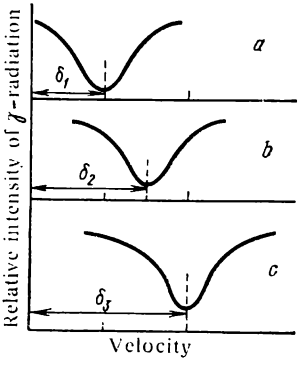


Fig. 97. Gamma-resonance absorption spectrum of (*a*) SnI_4, (*b*) $SnBr_4$, and (*c*) $SnCl_4$ (source of resonance radiation of ^{119}Sn in combination with SnO_2)

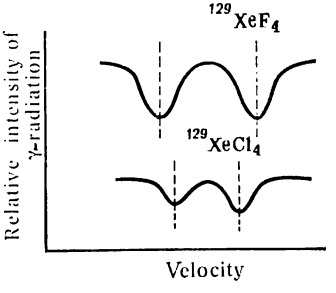


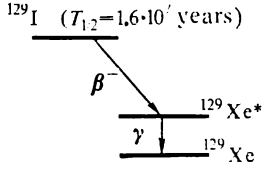
Fig. 98. Gamma-resonance absorption spectra of $XeCl_4$ and XeF_4 molecules

different energies are required to excite nuclear transitions depending on the type of compound. Since, however, the effect of the nature of the chemical vicinity of the atom on the shift in nuclear energy levels is insignificant, resonance absorption of gamma-quanta can be obtained by altering their energy, for which it is enough to move the source (or the absorber) of gamma-rays relative to the acceptor (source) of the radiation. This increases or decreases the energy of the gamma-quanta by the magnitude of the kinetic energy. At a certain speed of motion, resonance absorption begins, i.e. the

Mössbauer effect is observed. The Mössbauer effect, clearly, can only be observed with isotopes for which nuclear transitions induced by gamma-rays are possible.

An apparatus for studying gamma-absorption (Fig. 96) consists of a container *1* with the source of radiation (e.g. nuclei of ^{57}Fe, ^{119}Sn, ^{129}I, ^{129}Xe, ^{40}K, etc.), a container *2* with the test sample (the absorber of gamma-rays), and a recording unit *3* which measures the gamma-radiation transmitted through the absorber. The gamma-resonance absorption spectra of certain tin compounds are shown in Fig. 97. The speed of movement of the source of gamma-rays is plotted against the x-coordinate and the relative intensity of the transmitted radiation against the y-coordinate. Comparison of the spectrograms and the speeds of movement enables us to conclude that the degree of excitation of the tin atom in the series SnI_4—$SnBr_4$—$SnCl_4$ is increased, i.e. that the ionic character of the bond in this series is strengthened.

Let us consider another example of gamma-resonance spectroscopy. Figure 98 shows the gamma-spectra of $XeCl_4$ and XeF_4 molecules. Xenon tetrachloride cannot be obtained by ordinary chemical reactions, but it is formed during radioactive decay of the ^{129}I atom of the ICl_4^- ion (for example, in $KICl_4$):



$$^{129}_{53}I \rightarrow {}^{129}_{54}Xe + \beta^- + \gamma$$

or

$$ICl_4^- \rightarrow XeCl_4 + \beta^- + \gamma$$

The excited nuclei of ^{129}Xe so formed pass to the ground state through gamma-radiation. This makes it possible to obtain a gamma-resonance absorption spectrum (Fig. 98). The ICl_4^- ion has a square structure, which has also been discovered for the XeF_4 molecule. Comparison of the gamma-spectra of $XeCl_4$ and XeF_4 (Fig. 98) shows that the square structure is preserved after conversion of the ICl_4^- ion into a $XeCl_4$ molecule. Similar investigations made it possible to discover the oxides XeO_3 and XeO_4 which are formed during gamma-decay of the ^{129}I isotope in the compounds KIO_3 and KIO_4 respectively:

$$IO_3^- \rightarrow XeO_3 + \beta^- + \gamma$$
$$IO_4^- \rightarrow XeO_4 + \beta^- + \gamma$$

Thus gamma-spectroscopy enables us to assess the character of the distribution of electron density in compounds and to establish their structure. The method is very useful for studying the concentration and state of elements in ores and minerals, determining the intermediate stages of reactions, and so on.

CHAPTER 2

Diffraction Analysis

2.1. X-ray Crystallography

X-rays and fluxes of electrons or neutrons with wavelength of the same order as the distance between atoms in molecules or between atoms, ions, and molecules in crystals, are used in diffraction methods of investigating structure. In passing through a substance these rays are diffracted and the resultant diffraction pattern therefore corresponds strictly to the structure of the substance being investigated. X-rays (X-ray diffraction analysis) are mostly used to study the structure of crystals, electrons (electron diffraction analysis) to study gases and crystals, and neutrons (neutron diffraction analysis) to study liquids and solids.

The apparatus for X-ray diffraction analysis of the structure of crystals is shown in Fig. 99*a*. X-rays from the tube *1* are passed

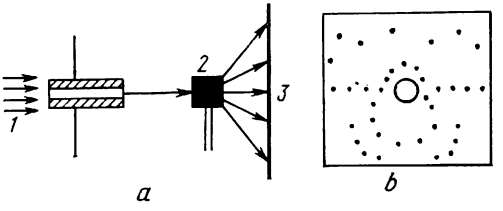


Fig. 99. Diagram (*a*) of the X-ray study of crystals and (*b*) of an X-ray diffraction pattern

through a diaphragm onto a crystal *2*. As they pass through the crystal they are reflected from the lattice points (electron shells of atoms, ions, or molecules), deflected, and form an interference pattern. This diffraction pattern is recorded on a photographic plate *3* in the form of spots corresponding to the maximum interference of the X-rays (Fig. 99*b*).

An *X-ray diffraction pattern* is really a kind of projection of the elements of the crystal lattice onto a photographic plate. The spatial arrangement of the particles in the crystal can be determined from the position of the spots on the plate. Interpretation of the pattern enables us to determine the parameters of the lattice and the bond lengths and effective radii of the particles forming the crystal.

X-ray diffraction patterns may have various forms (e.g. a combination of concentric lines and bands—see Fig. 100), depending

on the method of analysis employed. As will be seen from Fig. 100 the diffraction patterns of diamond and graphite differ sharply

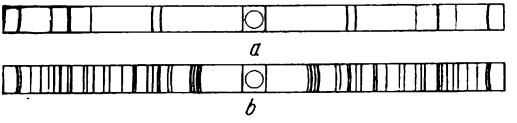


Fig. 100. X-ray diffraction patterns of (*a*) diamond and (*b*) graphite

from one another in the number of lines and bands, and the character of their distribution, which are due to the well-known marked difference in structure of these allotropic forms of carbon.

X-ray apparatus has now been developed that automatically interprets diffraction patterns and even produces a stereoscopic drawing of the structure of the substance being studied. This is done by reg-

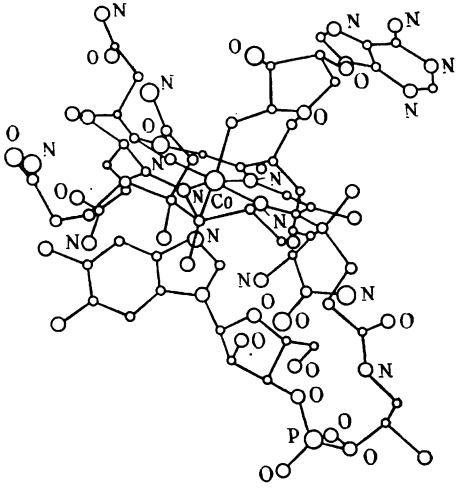


Fig. 101. Three-dimensional drawing of a molecule of vitamin B_{12} (as drawn by a computer)

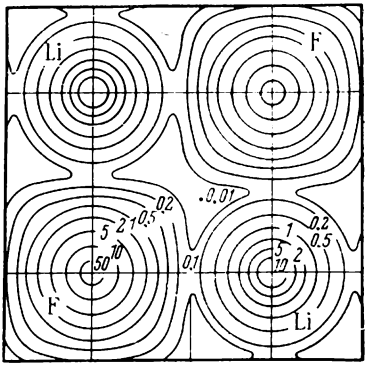


Fig. 102. Distribution of electron density in a crystal of LiF

istering the X-rays diffracted in its crystal lattice by means of a photocell. The pulses of the cell are automatically coded and fed into a computer, which produces a model of a possible structure from the data and then calculates the converse, i.e. calculates a diffraction pattern from the structure. If the calculated and experimental patterns do not coincide, changes are introduced automatically into the model and the back calculation repeated, and so on, until the maximum possible coincidence is obtained between the diffraction pattern and the model. The model can be

viewed on a cathode-ray tube, or the computer can produce a stereoscopic drawing (Fig. 101).

Diffraction patterns are analysed to ascertain the way electron density is distributed in a crystal. In this way we learn whether the crystal is ionic, covalent, or molecular. The distribution of electron density in a LiF crystal is shown in Fig. 102. The character of the curves of equal electron density (electron charge per unit volume) indicates a predominance of ionic bonds. The minimum density can be taken as the boundary between the Li and F atoms.

Atomic and ionic radii. Assuming provisionally that atoms and ions are spheres, the bond length d can be taken as the sum of the radii of two neighbouring particles. If both particles are identical, the radius of each will obviously be $1/2d$. Thus the atomic distance in a metallic crystal of sodium is 0.320 nm; hence its metallic atomic radius is 0.160 nm. The length in a molecule of Na_2 is 0.308 nm, i.e. the covalent radius of the sodium atom is 0.154 nm. In other words the atomic radii of one and the same element depend on the type of chemical bond. The magnitudes of covalent radii also depend on bond order. For example, the covalent atomic radii of carbon with single, double, and triple bonds are 0.077, 0.067 and 0.060 nm respectively.

The effective radii of atoms and ions in compounds are determined by the difference in the bond distance and the known effective radius of one of the particles involved. It has been established by various methods, for instance, that the ionic radius of the F^- ion is 0.133 nm. On the other hand, interpretation of the X-ray diffraction pattern of a crystal of NaF gives a value of $d = 0.231$ nm. The radius of the Na^+ is consequently 0.098 nm.

Effective atomic and ionic radii also depend on the characteristic coordination number of a given structure. While the radius of a metallic atom of Na, for instance, is 0.160 nm with a coordination number of eight, it is 0.189 nm with a coordination number of 12. As a rule, reference tables give the radii of metallic atoms for a coordination number 12 and of ions for a coordination number of six (NaCl type structure). A special contribution to the determination of atomic and ionic radii has been made by V. M. Goldschmidt, Linus Pauling, and N. V. Belov.

2.2. Electron and Neutron Diffraction Analysis

Figure 103 is a block diagram of an electron diffraction camera for studying the molecules of gases. A beam of electrons generated by strongly heating a metal filament *2* and accelerated by the difference of potentials *3* is passed through the chamber. Some molecules of the substance under investigation *1* are let into the same chamber. As electrons encounter the molecules they are diffracted. The result

is recorded on a photographic plate in the form of an *electron diffraction pattern.*

An electron diffraction pattern (Fig. 104) consists of a central sport and concentric rings of various density. The central spot is

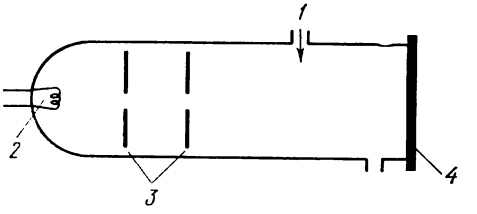


Fig. 103. Diagram of an electron diffraction instrument:
1—vapour of test substance; *2*—source of electrons; *3*—electron accelerator; *4*—photographic plate

caused by the undiffracted beam of electrons while the rings arise through the diffraction of electrons from the beam's initial direction.

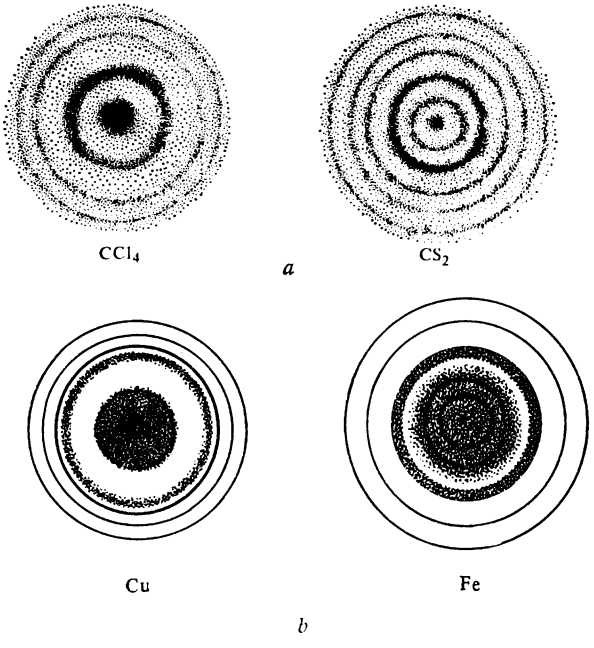


Fig. 104. Electron diffraction patterns of (*a*) gases and (*b*) crystals

Their character and intensity depend on the structure of the molecules concerned. Appropriate methods of interpreting patterns make

it possible to determine the configuration of the molecule, establish the arrangement of the atoms within it, and calculate valence angles and bond lengths. The results of the electron diffraction analysis of the structure of certain molecules are given in Table 15.

Table 15. **Structure of Selected Molecules**

Molecule	Bond length, nm	Valence angle	Molecular configuration
Cl_2	ClCl2.00	—	Dumb-bell
SO_3	SO1.43	OSO 120°	Planar triangle
BF_3	BF1.30	FBF 120°	ditto
$COCl_2$	CCl1.74 CO1.17	ClCCl 112°30′	ditto
PBr_3	PBr2.18	BrPBr 101°	Pyramidal
P_4	PP2.21	PPP about 60°	Tetrahedral
CCl_4	CCl1.75	ClCCl 109°28′	Tetrahedral
CS_2	CS1.554	SCS 180°	Linear

Electron beams are also used to study the structure of crystals. The substance in question is spread in a very thin layer on a plate through which an electron beam is then passed. The electron diffraction patterns of copper and iron foils, shown in Fig. 104*b*, display the difference in their structure (copper with a face-centred cubic lattice and iron with a body-centred cubic lattice).

Neutron diffraction analysis is also used to study the structure of crystals and liquids, its advantage (compared with the other diffraction methods) lies in the possibility of establishing the spatial position of hydrogen atoms, which is especially important for studying biological objects. It helps solve fundamental problems of molecular biology.

CHAPTER 3

Study of the Behaviour of Substances in Magnetic and Electric Fields

3.1. Magnetic Measurements

All substances are divided into two groups as regards their behaviour in an external magnetic field: *diamagnetic* and *paramagnetic*. Diamagnetic substances offer more resistance to the passage of magnetic lines of force than a vacuum, so that an external magnetic field

repels them. Paramagnetic substances, on the contrary, transmit magnetic lines of force better than a vacuum, so that a magnetic field tends to attract them. When diamagnetic substances are placed

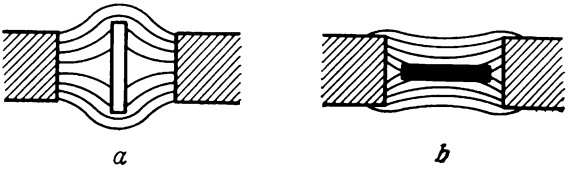


Fig. 105. Behaviour of (*a*) diamagnetic and (*b*) paramagnetic substances in a magnetic field

between the poles of a strong magnet, they are oriented perpendicularly (Fig. 105*a*), while paramagnetic substances assume a position along the lines of force (Fig. 105*b*).

The so different behaviour of diamagnetic and paramagnetic substances is due to the different character of their inner magnetic fields. The rotation of electrons about their axis (spin), we know, generates a magnetic field characterised by a spin magnetic moment. If the magnetic fields of electrons in a substance counterbalance each other and their net magnetic moment is zero, the substance is diamagnetic; when the magnetic fields do not counterbalance each other and the substance has a net magnetic moment, it is paramagnetic. The hydrogen atom, for example, having only one electron, is paramagnetic, while its molecule H_2 is diamagnetic since the electron spins are mutually balanced through the formation of a chemical bond.

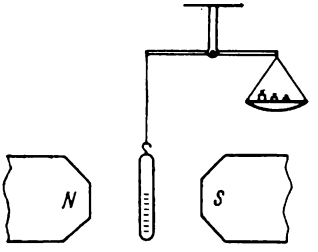


Fig. 106. Determination of magnetic susceptibility

The relation of a substance to an external magnetic field can be studied by the apparatus illustrated in Fig. 106. The test sample is placed in a glass ampoule and calibrated on a balance. The electromagnet is then switched on and the repulsion or attraction effect measured by again equilibrating the balance. The attraction of a paramagnetic substance in a magnetic field will obviously be greater, the more unpaired electrons there are in it. Study of magnetic properties thus makes it possible to determine the number of unpaired electrons in a substance and the distribution of electrons by orbitals.

3.2. Study of Dipole Moments

One way of establishing the dipole moment of molecules is based on measuring the substance's permittivity at various temperatures. To that end, the substance (in the form of a gas or a solution in a nonpolar solvent) is placed between the plates of a capacitor which increases the capacitance by ε times (ε being the dielectric constant). If the capacitance of the capacitor in a vacuum is C_0, and the capacitance of the substance C, then

$$\varepsilon = \frac{C}{C_0}$$

The rise in capacitance (through lowering the force of the electric field by ε times) is explained by the expenditure of energy on deformational polarisation of the molecules and their orientation in the field.

The deformational polarisation P_d observed irrespective of the type of molecule (polar or nonpolar) consists in a dipole moment being induced in the molecule by the electric field.

If the electric field is not very strong, we can assume that the induced dipole moment, μ_1, is proportional to the intensity of the electrical field E:

$$\mu_1 = \alpha E$$

where α is the *deformational polarisability*. The polarisability of a molecule is the higher, the easier its electron density is displaced relative to the nuclei.

The orientation of molecules by induced dipoles does not depend on temperature. If the position of a molecule is disturbed by thermal motion, a new dipole arises that is oriented in the same direction.

Another effect responsible for the rise in a capacitor's capacitance is displayed by polar molecules, i.e. molecules with a permanent dipole moment μ. The electric field tends to orient the molecules by their appropriate dipole ends toward the capacitor's positive and negative plates, an effect known as *orientation polarisation* P_0, which is the greater the bigger μ is. Orientation polarisation does depend on temperature, since heating intensifies the thermal motion of molecules and interferes with their orientation.

The total polarisation P of a substance is the sum of the orientation (P_0) and deformational (P_d) polarisation: $P = P_d + P_0$.

The rise in a capacitor's capacitance depends on molecules' polarity and polarisability, i.e. on their permanent μ_p and induced μ_1 dipole moments. The dependence of polarisability on temperature is due to the variation of P_0, i.e. ultimately by μ.

The dependence of P on $1/T$ for several molecules is shown in Fig. 107. The value of μ can be calculated from the slope of the lines. As will be seen from Fig. 107, the polarisation of benzene

and carbon dioxide does not depend on temperature; consequently the molecules of C_6H_6 and CO_2 are nonpolar. The polarisation of

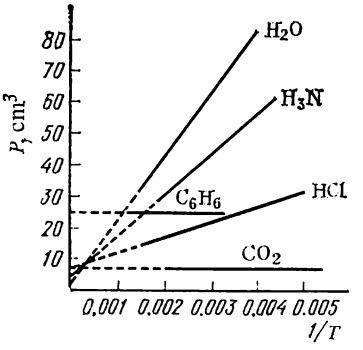


Fig. 107. Dependence of molecule polarisation on temperature

water, ammonia, and hydrogen chloride, on the contrary, depends on temperature, and the molecules of H_2O, H_3N, and HCl are therefore polar (see Table 9). The dipole moment in these compounds decreases as follows

$$\mu_{H_2O} > \mu_{H_3N} > \mu_{HCl}$$

Study of electric dipole moments enables us to judge the character of the distribution of electron density in a molecule, and its spatial structure and polarisability.

V

INTRODUCTION TO THE THEORY OF CHEMICAL PROCESSES

> The world is not to be apprehended as a complex of readymade *things*, but as a complex of *processes*, in which the things apparently stable ... go through an uninterrupted change.
>
> Frederick Engels, *Ludwig Feuerbach and the End of Classical German Philosophy*

> Chemical conversions, chemical reactions, are the main subject of chemistry. Study of the various properties of the elements and their compounds and, in particular, of the structure of atoms and molecules, really only provides chemists with supplementary material that makes their main task, rational control of the chemical conversion, easier. The deeper we go into the properties and structure of matter, and the more we know about them, the more confidently can the chemist proceed with synthesis.
>
> N. N. Semyonov

Chemical conversion is a qualitative leap in which some substances disappear and others are formed. The reconstruction of the electron structure of atoms, ions, and molecules taking place in it, is accompanied with an evolution or absorption of heat, light, electricity, etc., i.e. with a transformation of chemical energy into energy of another type.

The energy effect of reactions is studied by *thermochemistry*. Data on these changes are utilised to calculate the energy of interatomic and intermolecular bonds, to determine the structure and reactivity of substances, to establish the direction of chemical process, to calculate the energy balances of industrial processes, and so on.

The state of a system (substance or combination of substances) is described by several variables, viz., temperature, pressure, volume, mass. It is also important to know such properties of the system as its internal energy U, enthalpy H, entropy S, and Gibbs' free energy or function G, in order to characterise its state and the changes taking place in it. The energy effects of processes, in particular, can be judged from them.

CHAPTER 1

The Energy Relations of Chemical Conversions

1.1. Heat of Reaction

Chemical reactions proceed, as a rule, at a constant pressure (e.g. in an open flask) or in a constant volume (e.g. in an autoclave), i.e. are respectively isobaric or isochoric processes.

The energy effect of a chemical process arises from changes in the system of internal energy U or enthalpy H. The internal energy is the total energy, which is composed of the energy of the molecules' motion and interaction, and that of the nuclei and electrons in atoms, molecules, and crystals, intranuclear energy, etc. (i.e. all forms except the kinetic energy of the system as a whole and its potential energy by virtue of its position).

Let us assume that a system passes from state *1* to state *2* by absorbing a certain amount of heat Q. In the general case this heat will be expended on changing the system's internal energy ΔU and resisting external forces A:

$$Q = \Delta U + A$$

This equation expresses the law of conservation of energy*, i.e. means that the total change in a system's internal energy and the work done within (or applied to) it is equal to the heat absorbed by (or liberated from) it. If heat is transferred to the gas in a cylinder closed by a piston, for instance, the gas will (1) be heated (i.e. its internal energy U will increase) and (2) expand (i.e. will perform the work A of raising the piston).

In chemical reactions by work against external forces is mainly meant work against external pressure. As a first approximation (with p = constant) it is equal to the product of pressure p and the change in volume ΔV as the system passes from state *1* to state *2*:

$$A = p(V_2 - V_1) = p\Delta V$$

In an isochoric process (V = constant), A 0 since no change occurs in the system's volume. Its transition from state *1* to state *2* then corresponds to the equation:

$$Q_V = U_2 - U_1 = \Delta U$$

Thus, if a reaction proceeds in a constant volume, the liberation or absorption of heat Q_V is connected with changes in the system's internal energy.

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* The law of conservation of energy is also known as the *first law of thermodynamics.*

For an isobaric process (p = constant) the heat effect Q_p is

$$Q_p = \Delta U + p\,\Delta U, \quad Q_p = (U_2 - U_1) + p\,(V_2 - V_1)$$

or

$$Q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

Assuming that $U + pV \equiv H$, then $Q_p = H_2 - H_1 = \Delta H$.

The value H is called *enthalpy* which can be regarded as the energy of an expanded system. Thus, while the heat of reaction in an isochoric process is equal to the change in the system's internal energy, $Q_V = \Delta U$, in an isobaric process it is equal to the change in the system's enthalpy, $Q_p = \Delta H$.

The heat of a reaction taking place at constant pressure will differ from that of a reaction proceeding in a constant volume by a value $p\,\Delta V$. For an isobaric process, ΔV is the difference between the sum of volumes of the reaction products and the sum of the volumes of the reactants. Thus, for a reaction with the general formula

$$a\mathrm{A} + b\mathrm{B} + \ldots = d\mathrm{D} + e\mathrm{E} + \ldots$$

the changes in volume will be determined by the equation

$$\Delta V = \sum V_{\text{products}} - \sum V_{\text{reactants}} = (dV_\mathrm{D} + eV_\mathrm{E} + \ldots) - (aV_\mathrm{A} + bV_\mathrm{B} + \ldots),$$

where V_A, V_B, . . ., V_D, V_E . . . are molar volumes of substances A, B, . . ., D, E . . .; $\sum V_{\text{products}}$ is the sum of the molar volumes of the products; and $\sum V_{\text{reactants}}$ is the sum of the molar volumes of the reactants. Most chemical reactions occur at constant pressure; therefore we shall mainly be concerned with isobaric processes and will assess heat reaction by changes in the system's enthalpy.

1.2. Thermochemical Equations

The heat of reactions can be determined either experimentally, or by means of thermochemical calculations. We cannot, however, it should be noted, determine the absolute values of internal energy and enthalpy, but that does not affect the thermochemical calculation since we are interested in the heat effect of the *process*, i.e. the *change* in the system's state (viz., the change in the values of H and U).

In *exothermic* reactions heat is *liberated*, i.e. the enthalpy or internal energy of the system diminishes and ΔH and ΔU are negative. In *endothermic* processes heat is *absorbed*, i.e. the system's H and U increase and ΔH and ΔU have positive values.

In order to make the heat of various processes comparable, thermochemical calculations usually relate to one mole of a substance in *standard* conditions, i.e. a pressure of 101 325 Pa and a temperature of 25 °C (298.15 K). Standard heat effects are usually designated as ΔH°_{298} (ΔU°_{298}).

By the standard state of substances at a given temperature is meant: (a) for crystals and liquid substances their stable state at atmospheric pressure, and (b) for gases their state at atmospheric pressure, provided they behave like ideal gases (i.e. as if at very low pressures). For substances in solution, a concentration of one mol/litre is taken as standard, provided the solutions behave like ideal ones (i.e. of infinite dilution).

The equations of chemical reactions with an indication of the heat of reaction are called *thermochemical equations.* The thermochemical equation of a reaction in which one mole of water is synthesised is written as follows:

$$H_2(g) + 1/2\ O_2(g) = H_2O\ (l),\quad \Delta H^\circ_{298} = -286\ \text{kJ}$$

It also indicates the physical state of the reacting substances and their polymorphic variant. Thus the gaseous state is designated by the letter g, the liquid by the letter l, the crystalline by the letter c, the solid state by the letter s, a solution by the letters sol, and so on.

Hess's law. Thermochemical calculations are based on the law formulated by Germain Hess (1841), which states that the *total heat of a reaction depends solely on the type (nature) and state of the initial substances and the end products, but not on the course of the process, i.e. on the number and character of the intermediate stages.*

The formation of carbon (IV) dioxide from graphite and oxygen can be regarded either as the direct result of the interaction of simple substances:

$$C\ (\text{graphite}) + O_2(g) = CO_2(g),\ \Delta H_1$$

or as the result of a process taking place with an intermediate stage of the formation and combustion of carbon(II) monoxide:

$$C\ (\text{graphite}) + 1/2\ O_2(g) = CO\ (g),\quad \Delta H_2;$$
$$CO\ (g) + 1/2\ O_2(g) = CO_2\ (g),\ \Delta H_3$$

or, to summarise

$$C\ (\text{graphite}) + O_2\ (g) = CO_2\ (g),\ \Delta H_2 + \Delta H_3$$

In accordance with Hess's law, the heat changes in the formation of CO_2 are the same in either case (whether directly from the simple substances or through the intermediate stage of the formation and combustion of CO):

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

The process described can be shown graphically in the form of an *enthalpy diagram* (Fig. 108). The difference in the enthalpies of the reactants, and intermediate and end products of the reaction shown in the diagram corresponds to the heat of the corresponding reactions.

One can easily calculate one of the values ΔH, once the other two are known either from this enthalpy diagram or from the equation given above. The heat of formation of CO_2 (ΔH_1) and heat of combustion of CO (ΔH_3) can be determined experimentally, but it is impossible to determine the heat of formation of CO (ΔH_2) since the combustion product of graphite is a mixture of CO and CO_2 (combustion in conditions of oxygen deficit). But the heat of formation of CO can be calculated from the known values of ΔH_1 (—393.4 kJ/mol) and ΔH_3 (—282.9 kJ/mol):

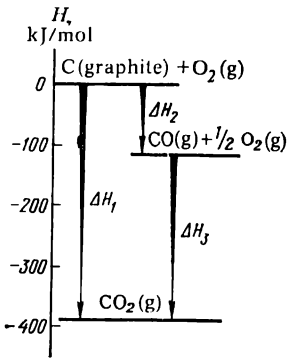


Fig. 108. Enthalpy diagram of the oxidation of graphite and CO

$$\Delta H_2 = \Delta H_1 - \Delta H_3 = -110.5 \text{ kJ}$$

Heat (enthalpy) of formation. The *enthalpy (heat) of formation* of substances is widely used in thermochemical calculations. By it is understood the thermal effect of a reaction forming one mole of a substance from simple substances. *Standard heats of formation* of simple substances are normally used, and designated as $\Delta H^\circ_{f,298}$ (one of the indices is often omitted). The heats of formation of simple substances that are stable in standard conditions (gaseous oxygen, liquid bromine, crystalline iodine, rhombic sulphur, graphite, etc.) are taken as zero. The standard enthalpies for selected substances are given in Table 16.

According to Hess's law, the heat of reaction equals the sum of the heats of formation of the products minus the sum of heats of formation of the reactants. The heat of reaction ΔH for a reaction of the form

$$aA + bB + \ldots = dD + eE + \ldots$$

is expressed by the following equation:

$$\Delta H = (d\,\Delta H_{f,D} + e\,\Delta H_{f,E} + \ldots) - (a\,\Delta H_{f,A} + b\,\Delta H_{f,B} + \ldots)$$

or

$$\Delta H = \sum \Delta H_{f,\text{ products}} - \sum \Delta H_{f,\text{ reactants}}$$

Thus, for the interaction between gaseous SO_3 and crystalline Al_2O_3

$$Al_2O_3\,(c) + 3SO_3\,(g) = Al_2(SO_4)_3\,(c)$$

the heat of reaction ΔH°_{298} (in standard conditions) is determined by the equation

$$\Delta H^\circ_{298} = \Delta H^\circ_{f,\,Al_2(SO_4)_3} - [\Delta H^\circ_{f,\,Al_2O_3} + 3\Delta H^\circ_{f,\,SO_3}]$$

Table 16. **Standard Heats (Enthalpies) of Formation ($\Delta H^\circ_{f,\,298}$) of Selected Substances**

Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol	Substance	$\Delta H^\circ_{f,\,298}$, kJ/mol
Al (g)	326.3	H_2O (l)	—285.83
Al^{3+} (sol)	—530.0	H_2SO_4 (l)	—814.2
Al_2O_3 (c)	—1676	K^+ (sol)	—251.2
$Al_2(SO_4)_3$ (c)	—3442.2	KCl (c)	—435.9
C (diamond)	1.828	$KClO_3$ (c)	—391.2
CH_4 (g)	—74.86	KNO_3 (c)	—493.2
CO (g)	—110.5	KOH (c)	—425.8
CO_2 (g)	—393.5	$MgSO_4$ (c)	—1301.4
$CaCO_3$ (c)	—1206.9	$MgSO_4 \cdot 7H_2O$ (c)	—3384
$CaCl_2$ (c)	—795.0	N (g)	472.8
CaF_2 (c)	—1214.6	NO (g)	90.25
CaO (c)	—635.5	NO_2 (g)	33
$Ca(OH)_2$ (c)	—986.6	NO_3^- (sol)	—207.5
Cl (g)	121.3	Na (g)	108.3
Cl^- (g)	—233.6	Na^+ (g)	606.1
Cl^- (sol)	—167.2	NaCl (c)	411.1
H (g)	217.98	NaOH (c)	425.6
H^+ (g)	1536.2	Na_2SO_4 (c)	1384.6
H^+ (sol)	0	O (g)	246.8
HBr (g)	—34.1	O_3 (g)	142.3
HCl (g)	—92.8	OH^- (sol)	—230.2
HF (g)	—270.9	S (monoclinic)	0.38
HI (g)	26.6	SO_2 (g)	—296.9
H_3N (g)	—46.19	SO_3 (g)	—396.1
HNO_3 (l)	—174.3	SO_3 (l)	—439.0
H_2O (g)	—241.82	ZnO (c)	—350.6

From the data in Table 16, the heat of this reaction is

$$\Delta H^\circ_{298} = (-3442.2) - [(-1676.0) + 3\,(-396.1)] = -577.9 \text{ kJ}$$

Let us consider two other examples of the calculation of heat of formation* (values of $\Delta H^\circ_{f,298}$ are given below the formulas)

$$\begin{array}{ccccc} CaCO_3\,(c) & = & CaO\,(c) & + & CO_2\,(g) \\ -1206 & & -635.9 & & -393.5 \end{array}$$

$$\Delta H^\circ_{298} = [(-635.5) + (-393.5)] - (-1206.9) = -177.9 \text{ kJ}$$

$$\begin{array}{ccccc} 2KClO_3\,(c) & = & 2KCl\,(c) & + & 3O_2\,(g) \\ 2\,(-391.2) & & 2\,(-435.9) & & 0 \end{array}$$

$$\Delta H^\circ_{298} = [2\,(-435.9) + 0] - 2\,(-391.2) = -89.4 \text{ kJ}$$

* Accurate values of $\Delta H^\circ_{f,\,298}$ have not been determined for all substances. Those cited in various sources are quite controversial and the results of calculations of ΔH may therefore also differ. (This holds also for ΔS and ΔG).

The heats of formation are now known for about 4000 substances, which enables chemists to calculate the heat of the most varied reactions.

Let us consider some examples of calculation of the heat effects of processes. The heat of dissolution of a substance $\Delta H^\circ_{\text{dissl}}$

$$\begin{gathered} \text{KOH (c)} = \text{K}^+ \text{ (sol)} + \text{OH}^- \text{ (sol)} \\ -425.8 \qquad -251.2 \qquad -230.2 \\ \Delta H_{\text{dissl}} = [(-251.2) + (-230.2)] - (-425.8) = -55.6 \text{ kJ} \\ \text{KNO}_3 \text{ (c)} = \text{K}^+ \text{ (sol)} + \text{NO}_3^- \text{ (sol)} \\ -493.2 \qquad -251.2 \qquad -207.5 \\ \Delta H^\circ_{\text{dissl}} = [(-251.2) + (-207.5)] - (-493.2) = 34.5 \text{ kJ} \end{gathered}$$

The heat (enthalpy) of phase transition (ΔH_{melt}, ΔH_{ev}, ΔH_{subl}) of

$$\begin{gathered} \text{Na (c)} = \text{Na (g)} \\ 0 \qquad 108.3 \\ \Delta H^\circ_{\text{subl}} = 108.3 - 0 = 108.3 \text{ kJ} \\ \text{SO}_3 \text{ (l)} = \text{SO}_3 \text{ (g)} \\ -439.0 \qquad -396.1 \\ \Delta H^\circ_{\text{cv}} = (-396.1) - (-439.0) = 42.9 \text{ kJ} \end{gathered}$$

The energy of dissociation of diatomic molecules into atoms (the energy of chemical bond $\Delta H^\circ_{\text{diss}} = E_{\text{bond}}$)

$$\begin{gathered} \text{Cl}_2 \text{ (g)} = 2\text{Cl (g)} \\ 0 \qquad 2\,(121.3) \\ \Delta H^\circ_{\text{diss}} = 2\,(121.3) - 0 = 242.6 \text{ kJ} \\ \text{NO (g)} = \text{N (g)} + \text{O (g)} \\ 90.25 \qquad 472.8 \qquad 246.8 \\ \Delta H^\circ_{\text{diss}} = 90.25 - (472.8 + 246.8) = -629.35 \text{ kJ} \end{gathered}$$

The energy of conversion of an atom into an ion (ionisation energy $\Delta H^\circ_{\text{ionis}} = I_{\text{ionis}}$; electron affinity, $\Delta H^\circ_{\text{ea}} = F_{\text{ea}}$).

$$\begin{gathered} \text{H (g)} = \text{H}^+ \text{ (g)} + e^- \\ 217.98 \qquad 1536.2 \\ \Delta H^\circ_{\text{ionis}} = 1536.2 - 217.98 = 1318.22 \text{ kJ} \\ \text{Cl (g)} + e^- = \text{Cl}^- \text{ (g)} \\ 121.3 \qquad -233.6 \\ \Delta H^\circ_{\text{ea}} = (-233.6) - 112.3 = -345.9 \text{ kJ} \end{gathered}$$

Thermochemical calculations can be used to determine the energy of chemical bonds, the energies of crystal lattices, the heat of intermolecular interactions, the enthalpy of dissolution and solvation (hydration), heats of phase transformations, etc.

Bond Energy. Bond energies can be used to calculate heats of reaction when the heat of formation of the substances involved in a reaction is not known. On the other hand, the heat of formation, sublimation, dissociation, and other energy effects are used to determine the strength of the interatomic, interionic and intermolecular bonds.

Let us calculate the energy of the H—Cl chemical bond ($E_{HCl} = -\Delta H_{H-Cl}$) in a molecule of HCl from the known enthalpy of formation of HCl ($\Delta H_{f,HCl} = -92.8$ kJ/mol) and the energy of dissociation of H_2 ($\Delta H_{diss} = 435$ kJ/mol) and Cl_2 ($\Delta H_{diss} = 243$ kJ/mol) into atoms.

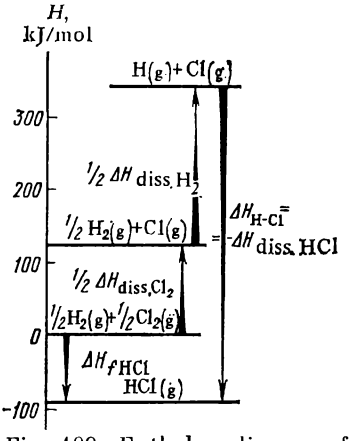


Fig. 109. Enthalpy diagram of the formation of HCl from the simple substances

The formation of HCl molecules from the simple substances can be mentally divided into two stages, namely, dissociation of the Cl_2 and H_2 molecules into atoms and the formation of HCl molecules from these atoms (Fig. 109):

$$1/2\ Cl_2\ (g) = Cl\ (g), \quad 1/2\ \Delta H_{diss}\ Cl_2$$
$$1/2\ H_2\ (g) = H\ (g), \quad 1/2\ \Delta H_{diss}\ H_2$$
$$H\ (g) + Cl\ (g) = HCl\ (g), \quad \Delta H_{H-Cl}$$
$$1/2\ H_2\ (g) + 1/2\ Cl_2\ (g) = HCl\ (g), \quad \Delta H_{f,\ HCl}$$

In accordance with Hess's law the algebraic sum of the heats of reaction of the intermediate stages in the formation of HCl from the simple substances equals the heat of formation of HCl:

$$1/2\ \Delta H_{diss\ Cl_2} + 1/2\ \Delta H_{diss\ H_2} + \Delta H_{H-Cl} = \Delta H_{f,\ HCl}$$
$$\Delta H_{H-Cl} = \Delta H_{f,\ HCl} - 1/2\ \Delta H_{diss\ Cl_2} - 1/2\ \Delta H_{diss\ H_2}$$
$$\Delta H_{H-Cl} = (-92.8) - (217.5 + 121.5) = -431.8\ kJ$$

i.e. the energy of the E_{H-Cl} bond = 431.8 kJ/mol.

The formation of hydrogen chloride from the simple substances is an exothermic process. As will be seen from the equation

$$\Delta H^\circ_{f,\ HCl} = \Delta H^\circ_{H-Cl} - (1/2\ \Delta H^\circ_{diss\ H_2} + 1/2\ \Delta H^\circ_{diss\ Cl_2})$$

the energy liberated during formation of H—Cl bonds in one mole of HCl (431.8 kJ/mole) is greater than the energy required to break the H—H and Cl—Cl bonds in a half-mole of H_2 (217.5 kJ) and a half-mole of Cl_2 (121.5 kJ).

Thus, reactions in which the end products have stronger bonds than the initial substances are exothermic. The conditions required for an endothermic reaction are, of course, exactly the opposite. The formation of NO from N_2 and O_2 is an endothermic process:

$$1/2\ N_2\ (g) + 1/2\ O_2\ (g) = NO\ (g), \quad \Delta H^\circ_{f,NO} = 90.3\ kJ/mol$$

As will be seen from Fig. 110, the energy required to break chemical bonds in a half-mole of N_2

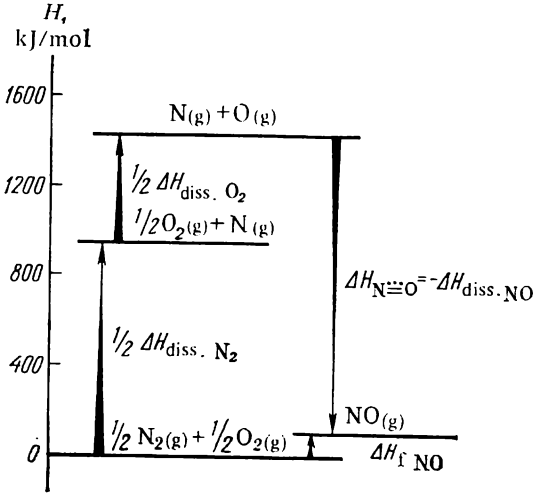


Fig. 110. Enthalpy diagram of the formation of NO from the simple substances

and in a half-mole of O_2 is greater than that liberated in formation of the end product, i.e. one mole of NO from the atoms.

Atomic heat of formation. The heat of a reaction by which a substance is formed from atoms is called the atomic heat (enthalpy) of formation. It is equal to the heat (enthalpy) of atomisation (with the sign reversed), i.e. the heat of decomposition of a given substance into free atoms. For a process with the general formula

$$AB_n = A + nB$$

the heat of atomisation of AB_n is equal to the difference between the sum of the enthalpies (a) of the atoms ($\Delta H_{f,A}$ and $\Delta H_{f,B}$) and (b) of the compound AB_n ($\Delta H_{f,AB_n}$):

$$\Delta H_{at\ AB_n} = (\Delta H_{f,A} + n\,\Delta H_{f,B}) - \Delta H_{f,B}$$

Knowing the heat of atomisation it is easy to calculate the mean energy of the E_{A-B} bond from the formula

$$E_{A-B} = \Delta H_{at\ AB_n}/n$$

For example, the energy (heat of atomisation) absorbed in the process

$$CH_4 = C + 4H$$

is 1642 kJ/mol. The mean energy of the C—H bond is then $E_{C-H} = 413$ kJ/mol.

Table 17. **Energy (U°_{298}) of Selected Crystal Lattices**

Lattice	Example	U°_{298}, kJ/mol	Lattice	Example	U°_{298}, kJ/mol
Ionic	LiF	1024	Molecular with	CH_4	10.0
	KOH	790.5	dispersion	H_2	1.004
	KNO_3	684.5	interaction		
Atomic-covalent	C (diamond)	715	with hydrogen	H_2O	50.2
	SiC	1250	bonds	HF	29.3
Atomic-metallic	K	89.2			
	Cr	397.5			

Lattice energy. The energy of a crystal lattice is the amount of energy required to break it down into its component parts and to separate them from one another to an infinitely great distance. The type and energy of the chemical bond in a substance can be determined from its lattice energy. The maximum energies are observed with lattices of ionic and ionic-covalent crystals, and the minimum ones with crystals with a molecular lattice (Table 17). Metals occupy an intermediate position as regards their lattice energies.

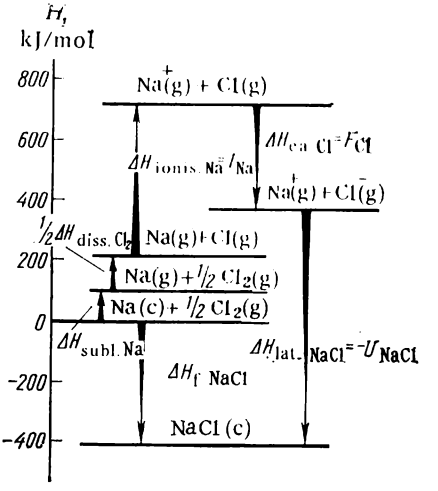


Fig. 111. Enthalpy diagram for calculating the lattice energy of NaCl (Born-Haber cycle)

When the gas formed during sublimation of a crystal consists of the same particles as the crystal itself, the lattice energy coincides with the energy of sublimation. This applies to molecular, atomic-covalent, and atomic-metallic crystals. Lattice energy can thus be determined experimentally.

At the same time, the energy of an ionic lattice cannot be determined experimentally since atoms or molecules are formed during sublimation of the ionic crystals. But the energy of an ionic lattice can be calculated from experimental findings of the energy characteristics of other processes by means of the *Born-Haber cycle.* For sodium chloride this cycle has the form of an enthalpy diagram (Fig. 111).

Crystalline sodium chloride (ionic lattice) is formed through the reaction of crystalline sodium with gaseous chlorine

$$Na\ (c) + 1/2\ Cl_2\ (g) = NaCl\ (c)$$
$$\Delta H^\circ_{298} = -411.1\ kJ$$

The heat of this process corresponds to the heat of formation of crystalline NaCl ($\Delta H^\circ_{f,298}$).

The formation of NaCl from the simple substances can also be shown as consecutive stages of obtaining gaseous ions Na^+ and Cl^- from crystalline sodium and gaseous molecular chlorine (see Fig. 111):

$$Na(c) \xrightarrow[\Delta H_{subl\ Na} = 108.3\ kJ/mol]{\text{sublimation (atomisation)}} Na(g) \xrightarrow[\Delta H_{ionis\ Na} = 495.8\ kJ/mol]{\text{ionisation}} Na^+(g)$$

$$Cl_2(g) \xrightarrow[1/2\,\Delta H_{diss\ Cl_2} = 121.3\ kJ/mol]{\text{dissociation (atomisation)}} Cl(g) \xrightarrow[\Delta H_{ea\ Cl} = 351.4\ kJ/mol]{\text{electron affinity}} Cl^-(g)$$

and their subsequent interaction to give ionic NaCl:

$$Na^+\ (g) + Cl^-\ (g) = NaCl\ (c), \quad \Delta H_{lat\ NaCl} = U_{NaCl}$$

According to Hess's law

$$U^\circ_{NaCl} = -\Delta H_{lat\ NaCl} = -\Delta H_{f,\ NaCl} + \Delta H_{subl\ Na} +$$
$$+ 1/2\,\Delta H_{diss\ Cl_2} + \Delta H_{ionis\ Na} + \Delta H_{ea\ Cl}$$

Substituting numerical quantities we get

$$U^\circ_{NaCl} = 785.1\ kJ/mol$$

The enthalpy diagram gives direct evidence of this (Fig. 111).

The lattice energy of ionic crystals can be calculated from the known enthalpy of formation of an ionic compound and the enthalpy of its constituent ions. For the example considered

$$NaCl\ (c) = Na^+\ (g) + Cl^-\ (g)$$
$$\Delta H^\circ_{lat} = \Delta H^\circ_{f,\ Na^+} + \Delta H^\circ_{f,\ Cl^-} - \Delta H^\circ_{f,\ NaCl}$$

$U^\circ_{NaCl} = 783.6$ kJ/mol (according to the values of ΔH°_f in Table 16).

Enthalpy (heat) of hydration of ions. The intensity of the interaction of the ions of a dissolved substance with water molecules can be characterised by the *enthalpy (heat) of hydration* ΔH_{hydr}, i.e. the amount of heat liberated during the transition of a mole of ions from vacuum into an aqueous solution.

The value of ΔH_{hydr} can be calculated from known values of the enthalpy of other processes. The dissolving of an ionic compound, for example, can be shown as two stages, viz., (a) breakdown of the crystal lattice into free ions and (b) hydration of the ions. According to Hess's law, the heat (enthalpy) of dissolution ΔH_{dissl} can then be represented as an algebraic sum of energies (enthalpies) of

the breakdown of the lattice ΔH_{lat} and the enthalpy of ion hydration ΔH_{hydr}:

$$\Delta H_{dissl} = \Delta H_{lat} + \Delta H_{hydr}$$

or

$$\Delta H_{hydr} = \Delta H_{dissl} - \Delta H_{lat}$$

Lattice energies are known for many ionic compounds; the heats of solution can be determined experimentally. Using the equation above the total enthalpy of hydration of cation and anion can be calculated. The enthalpy of hydration of a given ion is determined from the known enthalpy of hydration of an ion of opposite sign.

It can easily be guessed that enthalpy of hydration depends on the charge and size of the hydrated ion. In a series of ions the enthalpy of hydration increases with decreasing radius of the ions of similar electron configuration, e.g.:

	Li^+	Na^+	K^+	Rb^+	Cs^+
r, nm	0.068	0.098	0.133	0.149	0.165
ΔH°_{298}, kJ/mol	—531.4	—422.6	—338.9	—313.8	—280.3

and increasing charge of the ion, e.g.:

	Na^+	Mg^{2+}	Al^{3+}
r, nm	0.098	0.074	0.057
ΔH°_{hydr}, kJ/mol	—422.6	—1953.9	—4694.5

The breakdown of a lattice into free ions is an endothermic process ($\Delta H_{lat} > 0$); ion hydration is exothermic ($\Delta H_{hydr} < 0$). Thus, depending on the ratio of the values of ΔH_{lat} and ΔH_{hydr}, the heat of solution will be either positive or negative. The dissolving of crystalline potassium hydroxide is accompanied with liberation of heat, i.e. the energy required to break up the lattice of KOH ($\Delta H^\circ_{lat} = 790.5$ kJ/mol) is less than the amount liberated during hydration of the K^+ ions ($\Delta H^\circ_{hydr\,K^+} = -338.9$ kJ/mol) and the OH^- ions ($\Delta H^\circ_{hydr\,OH^-} = -510.5$ kJ/mol). The dissolution of crystalline potassium nitrate, on the contrary, is an endothermic process since the energy required to break up the lattice of KNO_3 ($\Delta H^\circ_{lat} = 684.5$ kJ/mol) is greater than that liberated during hydration of the K^+ and NO_3^- ions ($\Delta H^\circ_{hydr\,NO_3^-} = -309.6$ kJ/mol).

CHAPTER 2

Direction of Chemical Reactions

2.1. Entropy

Most processes are the result of two simultaneous phenomena: transfer of energy, and changes in the arrangement of particles relative to one another. A tendency to chaotic motion is inherent in particles (molecules, atoms, ions), so that a system tends to pass

from a more ordered state into a less ordered one. If a cylinder of compressed gas is connected to an empty vessel, for example, the gas will spread evenly throughout the vessel, so that the system changes from a more ordered (less disordered) state to a less ordered (more disordered) one. The quantitative measure of disorder is *entropy S*. In the transition of a system from a more ordered state to a less ordered one its entropy increases ($\Delta S > 0$).

The reverse transition (from a less ordered state to a more ordered one) is linked with a reduction of entropy, and the process is less likely to occur spontaneously. In the example above, it is thus clearly improbable that the system would spontaneously pass back from the vessel into the cylinder. When a system passes from a less ordered state to a more ordered one its entropy decreases ($\Delta S < 0$).

It is not difficult to show that entropy increases during the transition of a liquid to vapour, or when a crystalline substance dissolves, etc. In all these cases there is a reduction of order in the relative arrangement of the particles. In processes of condensation and crystallisation, on the contrary, entropy decreases.

Table 18. **Standard Entropy (S°_{298}) of Selected Substances**

Substance	S°_{298}, J/K·mol	Substance	S°_{298}, J/K·mol	Substance	S°_{298}, J/K·mol
Ag (c)	42.55	Fe (c)	27.15	NaCl (c)	72.12
AgBr (c)	107.1	FeS (c)	60.29	Na_2CO_3 (c)	136.4
AgCl (c)	96.11	Ge (c)	31.3	O (g)	160.9
AgI (c)	115.5	H^+ (sol)	0.00	O_2 (g)	205.04
Al (c)	28.35	H_2 (g)	130.52	O_3 (g)	238.8
AlSb (c)	69.03	HNO_3 (l)	156.6	OH^- (sol)	—10.86
$BaCO_3$ (c)	112.0	H_3N (g)	192.6	P (white)	41.1
$BaCl_2$ (c)	126.0	H_2O (g)	188.72	P (red)	22.7
$Ba(NO_3)_2$ (c)	214	H_2O (l)	70.08	Pb (c)	64.8
$BaSO_4$ (c)	132.0	H_2O (c)	39.33	S (g)	167.7
C (diamond)	2.368	H_2SO_4 (l)	156.9	S_2 (g)	228.18
C (graphite)	5.740	KCl (c)	82.56	S_6 (g)	377
CO (g)	197.54	$KClO_3$ (c)	142.97	S_8 (g)	444.2
CO_2 (g)	213.68	KOH (c)	79.32	SO_2 (g)	248.1
CH_4 (g)	186.19	$MgCO_3$ (c)	65.7	SO_3 (l)	122.05
$CaCl_2$ (c)	113.6	MgO (c)	26.9	Sb (c)	45.69
$CaCO_3$ (c)	92.9	N_2 (g)	199.9	Si (c)	18.8
CaO (c)	39.7	NH_4NO_3 (c)	151.0	SiO_2 (c)	42.7
Cl^- (sol)	56.54	NO (g)	210.6	SiO_2 (vit)	46.9
Cl_2 (g)	222.9	NO_2 (g)	240.2	Sn (c)	51.6
CrO_3 (c)	71.96	N_2O_5 (c)	178.4	ZnO (c)	43.64
Cr_2O_3 (c)	27.15				

The probability of the various states of a substance (gas, crystal, liquid) can be described as a certain property of it and quantitatively expressed as a value of entropy S in J/K·mol (J/deg·mol). The entropy of substances (like their enthalpy) is normally related to a temperature of 25 °C (298.15 K) and a pressure of 101 325 Pa. In these conditions it is designated as S°_{298} and is referred to as *standard entropy*. Table 18 gives standard entropies for selected substances.

In accordance with their degree of disorder, the entropy of substances is much higher in the gaseous state than in the liquid, and especially in the crystal, state. The standard entropy S°_{298} of water, for example, is 70.08 J/K·mol and of water vapour 188.72 J/K·mol. The entropy of amorphous substances is greater than that of crystalline substances (more ordered state). The standard entropies of vitreous and crystalline SiO_2, for example, are 46.9 and 42.7 J/K·mol, respectively. The standard entropy of graphite (5.740 J/K·mol) is higher than that of diamond (2.368 J/K·mol), which has a particularly rigid structure. For a given physical state the entropy is the higher, the more atoms there are in a molecule. The entropy O_3 (gas) is higher than that of gaseous O_2 and O (238.8, 205.04 and 160.9 J/K·mol, respectively).

Entropy values are used to determine changes in the entropy of a system involved in chemical conversions. Thus, for a chemical reaction

$$aA + bB + \ldots = dD + eE + \ldots$$

the change in the system's entropy will be

$$\Delta S = (dS_D + eS_E + \ldots) - (aS_A + bS_B + \ldots)$$

or

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

The changes of entropy in chemical reactions can be judged from the changes in the system's volume during the reaction. For example, in the reaction

$$1/2\ C\ (\text{graphite}) + 1/2\ CO_2\ (g) = CO\ (g), \quad \Delta S^\circ_{298} = 87.8\ \text{J/K}$$

there is an increase of volume ($\Delta V > 0$); consequently the entropy is higher ($\Delta S > 0$). But during formation of ammonia from hydrogen and nitrogen

$$3/2\ H_2\ (g) + 1/2\ N_2\ (g) = H_3N\ (g), \quad \Delta S^\circ_{298} = -103.1\ \text{J/K}$$

the system's volume, on the contrary, decreases ($\Delta V < 0$); consequently its entropy decreases ($\Delta S < 0$).

When a reaction proceeds between solids, e.g.

$$Al\ (c) + Sb\ (c) = AlSb\ (c), \quad \Delta S^\circ_{298} = -5.01\ \text{J/K}$$

there is practically no alteration of the system's volume and entropy. The same holds for processes in which the number of moles of gaseous substances is not changed, for example,

$$C\ (graphite) + O_2\ (g) = CO_2\ (g), \qquad \Delta S^\circ_{298} = 2.9\ J/K$$

The entropy of a compound (S°_{298}) is not equal to the change in entropy associated with the reaction of its formation from the simple substances ($\Delta S^\circ_{f,\,298}$). Thus, for a reaction

$$A + B = AB$$

we have

$$\Delta S^\circ_{f,\,298} = S^\circ_{AB} - (S^\circ_A + S^\circ_B)$$

The entropy of formation of a compound, $\Delta S^\circ_{f,\,AB}$, consequently differs from its entropy S°_{AB} because the values of entropy of simple substances, S°_A and S°_B are not zero in standard conditions.

The tendency of a system to increase its entropy is called the *entropy factor*. This factor is the stronger, the higher the temperature. It can be assessed quantitatively by the product $T\ \Delta S$ and expressed in units of energy (J).

A system's tendency to reduce its potential energy is called the *energy* or *enthalpy factor*. It is quantitatively expressed through the heat of the process, i.e. by the value of ΔH.

2.2. Gibbs' Free Energy

A system can only pass spontaneously, i.e. without external energy, from a less stable state to a more stable one. It follows from the discussion above that two tendencies operate simultaneously in chemical processes, to wit: (a) the tendency of particles to unite in more complicated ones through stable bonds, which *lowers* the system's *enthalpy*, and (b) their tendency to separate, which *raises entropy*. In other words, two opposite factors, enthalpy (ΔH) and entropy ($T\ \Delta S$), operate simultaneously. Their overall effect at constant T and p, reflects the change in *Gibbs' free energy* G*

$$\Delta G = \Delta H - T\ \Delta S$$

The character of changes in Gibbs' free energy enables us to judge whether or not a given reaction is feasible. The condition of the feasibility in principle of a process is the inequality $\Delta G < 0$.

In other words, a reaction can occur spontaneously if Gibbs' free energy of the initial system is higher than the system's energy

* J. W. Gibbs (1839-1903) was one of the founders of modern chemical thermodynamics. Gibbs' free energy is also referred to simply as *free energy*, or as *Gibbs' function*, or *thermodynamic potential*.

According to $\Delta H = \Delta G - T\Delta S$, the last term ($T\Delta S$) is part of the heat expended to increase disorder (i.e. uselessly dissipated in the medium). In contrast to the free energy, it cannot perform work and is therefore called bound energy.

at the end of the reaction. The increase in the free energy G

$$\Delta G > 0$$

indicates that a process cannot possibly occur spontaneously in the given conditions. If, however,

$$\Delta G = 0$$

the system is at the state of chemical equilibrium.

The enthalpy and entropy factors and direction of a process. In accordance with the equation

$$\Delta G = \Delta H - T\,\Delta S$$

the spontaneity of a process is promoted by a lessening of the system's enthalpy and raising of its entropy, i.e. when $\Delta H < 0$ and $\Delta S > 0$.

With other combinations of the character of the changes in H and S, the feasibility of a process depends either on the enthalpy or on the entropy factor. Consider the following two reactions:

$$CaO\ (c) + CO_2\ (g) = CaCO_3\ (c)$$
$$\Delta H^\circ_{298} = -178.0\ \text{kJ}$$
$$\Delta S^\circ_{298} = -160.48\ \text{J/K}$$
$$\Delta G^\circ_{298} = -190.2\ \text{kJ}$$
$$CaCO_3\ (c) = CaO\ (c) + CO_2\ (g)$$
$$\Delta H^\circ_{298} = 178.0\ \text{kJ}$$
$$\Delta S^\circ_{298} = 160.48\ \text{J/K}$$
$$\Delta G^\circ_{1500} = -62.7\ \text{kJ}$$

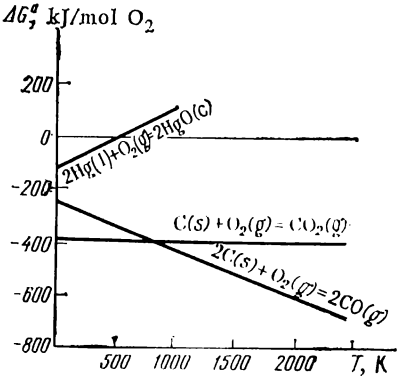


Fig. 112. Dependence of ΔG° on temperature in selected reactions

The first reaction is exothermic and the volume of the reactants decreases. The feasibility of this reaction ($\Delta G < 0$) is determined by the enthalpy factor, which exceeds the counteraction of the entropy factor (by the absolute value $|\Delta H| > |T\,\Delta S|$).

The second reaction is endothermic, and proceeds with an increase in volume. Its feasibility ($\Delta G < 0$), on the contrary, depends on the entropy factor. At high temperatures the entropy factor exceeds the enthalpy factor (i.e. $|\Delta H| < |T\,\Delta S|$) and the reaction proceeds spontaneously.

The effect of temperature on the direction of a process. According to the equation

$$\Delta G = \Delta H - T\,\Delta S$$

the effect of temperature on ΔG is determined by the sign and the magnitude of ΔS. The dependence of the ΔG of certain reactions

on temperature* is shown in Fig. 112. For a reaction with the equation

$$2C\ (graphite) + O_2\ (g) = 2CO\ (g), \quad \Delta S > 0$$

which is accompanied with a rise in entropy, raising of the temperature increases the negative value of ΔG. High temperatures favour the process. For the reaction

$$2Hg\ (l) + O_2\ (g) = 2HgO\ (c), \quad \Delta S < 0$$

which proceeds with a lowering of entropy the negative value of ΔG decreases with rising temperature. Hence a rise in temperature inhibits the reaction in this case. At the appropriate temperature, ΔG becomes positive and the reaction will proceed in the reverse direction. As will be seen from Fig. 112, the sign of ΔG reverses at 500 K in this reaction. Above this temperature the direction of the reaction is reversed:

$$2HgO\ (c) = 2Hg\ (l) + O_2\ (g), \quad \Delta S > 0$$

Thus, mercury is oxidised by oxygen at low temperatures (under 500 K) while at high temperatures (above 500 K) mercury oxide is decomposed with liberation of oxygen. These processes can be used to obtain oxygen in the laboratory.

If the entropy of a system does not change during a process, the value of ΔG does not in practice depend on temperature. Thus, for a reaction

$$C\ (graphite) + O_2\ (g) = CO_2\ (g), \quad \Delta S \cong 0$$

the dependence $\Delta G = f(T)$ is shown in Fig. 112 by a straight line that is practically parallel to the axis of abscissae.

Processes taking place with a lowering of enthalpy ($\Delta H < 0$) and a rise in entropy ($\Delta S > 0$) are *irreversible* in practice. The value of ΔG will then always be negative whatever the temperature.

Irreversible processes include, for example, the decomposition of potassium chlorate (V):

$$2KClO_3\ (c) = 2KCl\ (c) + 3O_2\ (g)$$

$$\Delta H^\circ_{298} = -89.2\ kJ, \quad \Delta S^\circ_{298} = 494.3\ J/K$$

Standard free energy of formation. The standard free energy of formation ΔG°_f is the change of free energy during the formation of one mole of a substance in standard conditions from simple substances each of which is also in standard conditions. This definition implies that the standard free energy of formation of a simple substance that is stable in standard conditions is zero.

* If the effect of temperature on ΔH and ΔS is disregarded, the above dependence $\Delta G = f(T)$ is the equation of a straight line whose slope is determined by the sign of ΔS. As will de seen from Fig. 112, the line slopes down with $\Delta S > 0$, anb up with $\Delta S < 0$.

The change in free energy, like the change in a system's enthalpy and entropy, does not depend on the path of the process. Therefore, for a reaction of the type

$$aA + bB + \ldots = dD + eE + \ldots$$

the change in standard free energy ΔG° is the difference between the sum of standard free energies of formation of the products and the sum of the standard energies of formation of the reactants:

$$\Delta G^\circ = (d\Delta G^\circ_{f,D} + e\,\Delta G^\circ_{f,E} + \ldots) - (a\,\Delta G^\circ_{f,A} + b\,\Delta G^\circ_{f,B} + \ldots)$$

or

$$\Delta G^\circ = \sum \Delta G^\circ_{f,\text{ products}} - \sum \Delta G^\circ_{f,\text{ reactants}}$$

Table 19. **Standard Gibbs' Energy of Formation ($\Delta G^\circ_{f,298}$) of Selected Substances**

Substance	$\Delta G^\circ_{f,298}$, kJ/mol	Substance	$\Delta G^\circ_{f,298}$, kJ/mol
Al (g)	288.7	H_2O (l)	—237.24
Al^{3+} (sol)	—490.5	H_2SO_4 (l)	—814.2
Al_2O_3 (c)	—1582	K^+ (sol)	—281.3
$Al_2(SO_4)_3$ (c)	—3101	KCl (c)	—408.0
Ba^{2+} (sol)	—561.1	$KClO_3$ (c)	—289.9
$BaSO_4$ (c)	—1353.0	KNO_3 (c)	—393.1
C (diamond)	2.833	KOH (c)	—380.2
CO (g)	—137.14	$MgSO_4$ (c)	—1158.7
CO_2 (g)	—394.38	$MgSO_4 \cdot 7H_2O$ (c)	—2868
$CaCl_2$ (c)	—750.2	N (g)	455.5
$CaCO_3$ (c)	—1128.8	NO (g)	86.58
CaF_2 (c)	—1161.9	NO_2 (g)	51.5
CaO (c)	—604.2	NO_3^- (sol)	—111.7
$Ca(OH)_2$ (c)	—896.8	Na (g)	77.3
Cl (g)	105.3	Na^+ (g)	575.6
Cl^- (c)	—239.9	NaCl (c)	—384.0
Cl^- (sol)	—131.4	NaOH (c)	—380.7
H (g)	203.3	Na_2SO_4 (c)	—1266.8
H^+ (g)	1516.99	O (g)	231.8
H^+ (sol)	0	O_3 (g)	162.7
HBr (g)	—53.2	OH^- (sol)	—157.4
HCl (g)	—94.79	S (monoclinic)	0.188
HF (g)	—272.8	SO_2 (g)	—300.2
HI (g)	1.78	SO_3 (g)	—370.0
H_3N (g)	—16.71	SO_3 (l)	—368.04
HNO_3 (l)	—80.3	SO_4^{2-} (sol)	—744.93
H_2O (g)	—228.61	ZnO (c)	—320.7

Using the data in Table 19, we can calculate ΔG°_{298} for the reaction

$$\begin{array}{ccc} NO\ (g) + 1/2\ O_2\ (g) = & NO_2\ (g) \\ 86.58 \qquad 0 & 51.5 \end{array}$$

$$\Delta G^{\circ}_{298} = \Delta G^{\circ}_{f,\ NO_2} - (\Delta G^{\circ}_{f,\ NO} + 1/2\ \Delta G^{\circ}_{f,\ O_2})$$

Substituting the values of ΔG°_{f} (placed under the symbols of the substances in the reaction equation), we get

$$\Delta G^{\circ}_{298} = 51.5 - (86.58 + 0) = -35.08\ \text{kJ}$$

The value of ΔG°_{298} found means that the formation of one mole of NO_2 in standard conditions, i.e. at $p_{NO} = p_{O_2} = p_{NO_2} = 101.3$ kPa, and a total pressure of 303.9 kPa, would be accompanied with a decrease in the system's free energy of 35.08 kJ/mol of NO_2 at 298 K.

When values of the standard free energy are used, the condition that $\Delta G^{\circ} \ll 0$ must be taken as the criterion of the feasibility of the process in nonstationary conditions and the inequality $\Delta G^{\circ} \gg 0$ as the criterion of its *infeasibility in principle*. If $\Delta G^{\circ} = 0$, of course, it does not mean at all that the system will be in a state of equilibrium in real conditions. The values of ΔG° can thus be used in many cases simply to assess a reaction's direction.

CHAPTER 3

Chemical Equilibrium

3.1. Equilibrium Constant

Most chemical reactions are *reversible*, i.e. they proceed in opposite directions simultaneously. Consider the reversible reaction

$$2H_2\ (g) + O_2\ (g) \rightleftarrows 2H_2O\ (g); \quad \Delta H < 0, \quad \Delta S < 0$$

When it proceeds directly, heat is liberated ($\Delta H < 0$). The entropy of the system falls ($\Delta S < 0$) because three moles of the gases form two moles of gas as a result of this reaction. The motive force is thus the energy (enthalpy) factor.

When the reaction proceeds in the reverse direction, heat is absorbed ($\Delta H > 0$). The entropy of the system rises ($\Delta S > 0$). The motive force is thus the entropy factor.

Imagine that a mixture of oxygen and hydrogen is introduced into a closed vessel at 2000 °C and 101.3 kPa. Water vapour will be formed. The reaction depends on the enthalpy factor. But as water vapour is formed, the entropy factor begins to operate and some of the vapour is decomposed into hydrogen and oxygen. At first the enthalpy factor prevails over the entropy factor, but their

effects operating in opposite direction will finally balance out: $\Delta H = T\,\Delta S$, i.e. $\Delta G = 0$. Chemical equilibrium will be reached in the system, and the number of molecules (or other particles) formed in the direct reaction in a unit of time is equal to the number of molecules (or other particles) that interact in the reverse reaction, i.e. chemical equilibrium is *dynamic*. At a state of chemical equilibrium *the rate of the direct reaction is equal to that of the reverse reaction.*

Thus, owing to the reversibility of the process, hydrogen and oxygen do not turn completely into water, and a mixture of all the three gases (hydrogen, oxygen, water vapour) is present simultaneously in the vessel. This observation can be summarised as follows: chemical reactions proceed spontaneously to a definite point, i.e. to the establishment of chemical equilibrium in the system ($\Delta G = 0$). Equilibrium can be reached from opposite aspects, i.e. through the interaction both of the reactants and of the products of the reaction.

As soon as equilibrium has been reached, the concentrations of the substances (both the reactants and the products) remain unchanged provided the conditions are not altered. These concentrations are called *equilibrium* concentrations.

Chemical reactions differ in the degree to which they proceed. Some reactions proceed practically to the end in given conditions, but others to very slight degree. Compare how far the synthesis of water vapour from the simple substances and decomposition of water into the simple substances proceed at 2000 °C and 101.3 kPa. It has been established experimentally that in these conditions an initial mixture of one mole of H_2 and 0.5 mole of O_2 forms 0.994 mole of water, 0.006 mole of hydrogen, and 0.003 mole of oxygen when chemical equilibrium has been attained. The ratio of the concentrations of the components will be the same if a mole of water is introduced. Thus, at 2000 °C and 101.3 kPa, the reaction synthesising water vapour is completed in practice, while the decomposition of water is to all intents and purposes negligible.

The law of mass action. The degree to which a reaction will proceed can be judged from the *law of mass action* that a system in a state of equilibrium obeys: *the quotient from dividing the product of the equilibrium concentrations of the reaction products by the product of the equilibrium concentrations of the initial substances is a constant* (Guldberg and Waage, 1864-7). This value is known as the *equilibrium constant* (symbol K).

For a reaction with the general equation

$$aA + bB + \ldots \rightleftharpoons dD + eE + \ldots$$

the following ratio holds in a state of equilibrium

$$K = \frac{[D]^d\,[E]^e\,\ldots}{[A]^a\,[B^b]\,\ldots}$$

where [A], [B], . . ., [D], [E], . . . are the equilibrium concentrations of substances A, B, . . ., D, E, . . .; and a, b, . . ., d, e, . . . are exponents of the degree of concentration of the given substances numerically equal to their coefficients in the formula of the reaction.

Values of K are calculated or found experimentally. Let us consider an equilibrium system

$$H_2\,(g) + I_2\,(g) \rightleftarrows 2HI\,(g)$$

at 698 K (425 °C). Experimentally found equilibrium concentrations of its components are given in Table 20. The initial mixture in the first five experiments was one of H_2 and I_2 in various proportions. In the last three experiments HI was taken as the initial substance. The figures show that in a state of equilibrium, the ratio of the concentrations of the components is constant and does not depend on them:

$$K_{698} = \frac{[HI]^2}{[H_2]\,[I_2]} = 54.441$$

Table 20. **Equilibrium Concentrations for the Reaction $H_2 + I_2 \rightleftarrows 2HI$ at 425 °C**

Experiment	Equilibrium concentration, mol/litre			$K = \frac{[HI]^2}{[H_2][I_2]}$
	H_2	I_2	HI	
1	1.8313×10^{-3}	3.1292×10^{-3}	17.671×10^{-3}	54.491
2	1.2523×10^{-3}	2.3360×10^{-3}	16.850×10^{-3}	53.964
3	2.9070×10^{-3}	1.7069×10^{-3}	16.482×10^{-3}	54.748
4	3.5600×10^{-3}	1.2500×10^{-3}	15.588×10^{-3}	54.604
5	4.5647×10^{-3}	0.7378×10^{-3}	13.544×10^{-3}	54.468
6	0.4789×10^{-3}	0.4789×10^{-3}	3.531×10^{-3}	54.455
7	0.4953×10^{-3}	0.4953×10^{-3}	3.655×10^{-3}	54.455
8	1.1409×10^{-3}	1.1409×10^{-3}	8.410×10^{-3}	54.337
			The mean value	54.441

The equilibrium partial pressures of the reactants are often used instead of their concentrations to express the equilibrium state during an interaction between gaseous substances *:

$$K_p = \frac{p_D^d p_E^e \cdots}{p_A^a p_B^b \cdots}$$

* The ratio of the equilibrium constants expressed through equilibrium concentrations of the reactants K_c, and through their partial pressures K_p is $K_p = K_c\,(RT)^{\Delta n}$, where Δn is the change in the number of moles of gases during the reaction. For a reaction in which the number of moles of gases does not change, $\Delta n = 0$ and $K_p = K_c$.

For the reaction above

$$K_p = \frac{p^2_{HI}}{p_{H_2} p_{I_2}}$$

The equilibrium constant is an important characteristic of a reaction. The direction of the process given the initial ratio of the reactants' concentrations, and the maximum possible yield of the reaction product in the given conditions can be judged from its value.

Effect of temperature on the equilibrium constant. The equilibrium constant depends both on the nature of the reactants and the temperature, and is linked with changes in the standard free energy of a reaction ΔG° by the equation

$$\Delta G^\circ = -RT \ln K$$

This equation* can be used to calculate K from ΔG° with subsequent calculation of the equilibrium concentrations (partial pressures) of the reactants. High negative values of ΔG° ($\Delta G^\circ \ll 0$) correspond to high values of K ($K \gg 1$), i.e. the products of the interaction prevail in a balanced mixture, with high positive values of ΔG° ($\Delta G^\circ \gg 0$) the initial substances prevail in a balanced mixture ($K \ll 1$). Assuming that

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ = -RT \ln K$$

then, after a certain conversion, we get

$$K = e^{-\frac{\Delta H^\circ}{RT}} e^{\frac{\Delta S^\circ}{R}}$$

It follows from this equation that the equilibrium constant is very sensitive to temperature changes, increasing in endothermic processes and decreasing in exothermic ones. It does not depend on pressure unless the latter is very high.

The equilibrium constant's dependence on the enthalpy and entropy factors indicates that it also depends on the nature of the reactants.

3.2. Le Chatelier's Principle

A state of chemical equilibrium persists for any time in the given conditions, but if these are altered the balance will be upset. The effect exerted on a system in equilibrium by any external action (e.g. a change in the concentration of the reactants, pressure, or temperature) can be predicted from *Le Chatelier's rule* (*the principle of dynamic equilibrium*):

if a system in equilibrium is subjected to an external effect, the balance will be upset in that direction of the process which will tend to weaken this effect.

* ΔG°_{298} (kJ) = — 5.71 log K_{298}.

Thus, according to Le Chatelier's principle, additional quantities of any reactant will shift equilibrium in a direction that will reduce the concentration of this substance and correspondingly increase that of its interaction products. Suppose oxygen is added to a system in equilibrium

$$2CO\ (g) + O_2 \rightleftarrows 2CO_2\ (g)$$

$$K = [CO_2]^2/[CO]^2\,[O_2]$$

The extra oxygen will intensify the formation of carbon(IV) oxide, which will continue until the system is again in a state of equilibrium. When the new equilibrium is reached the concentrations (partial pressures) of all reactants will differ from the initial ones but the ratio between them, expressed by the equilibrium constant will not be altered. In other words the concentration of any of the reactants in a system in equilibrium cannot be changed without changing the concentration of all others.

A change of pressure will upset equilibrium if the reaction is accompanied with a change in the volume of the system. In accordance with Le Chatelier's principle, an increase in pressure will shift chemical equilibrium toward the reaction that will reduce the system's volume. When pressure is reduced, the relation is reversed. For example, for a system in equilibrium (at 298 K)

$$\underset{\text{One volume}}{N_2O_4(g)} \rightleftarrows \underset{\text{Two volumes}}{2NO_2(g)}, \qquad K = \frac{[NO_2]^2}{[N_2O_4]}$$

the degree of dissociation of N_2O_4 at 50.6 kPa is 25.7 per cent. A doubled pressure (101.3 kPa) will reduce the degree of dissociation of N_2O_4 to 18.5 per cent. In other words, an increase in pressure shifts equilibrium toward the process by which NO_2 is converted into N_2O_4, i.e. in the direction of the reaction proceeding with a reduction of volume.

Since the condition $\Delta H = T\,\Delta S$ holds for a state of equilibrium, a change in temperature will lead to a change in ΔH. A rise in the temperature of a system will intensify operation of the entropy factor ($T\,\Delta S > 0$), i.e. the endothermic process will be intensified. A fall in temperature, on the contrary, will weaken the role of the entropy factor, i.e. the exothermic process will become more pronounced. According to Le Chatelier's principle, a rise in temperature shifts chemical equilibrium toward the process in which heat is absorbed, while a drop in temperature acts in the opposite direction. In the examples of equilibrium systems considered above

$$2CO\ (g) + O_2\ (g) \rightleftarrows 2CO_2\ (g), \qquad \Delta H < 0$$

$$N_2O_4\ (g) \rightleftarrows 2NO_2\ (g), \qquad \Delta H > 0$$

a rise in temperature will decompose CO_2 and N_2O_4 respectively while a drop in temperature will, on the contrary, promote synthesis of CO_2 and N_2O_4.

Study of chemical equilibrium is of great practical and theoretical importance. By determining the equilibrium position at various temperatures and pressures, we can select the conditions most advantageous for carrying out a chemical process. The final choice of conditions allows for their effect on the velocity of the process. Those conditions are needed that will ensure the maximum possible yield of end products (shifting of chemical equilibrium), at their fastest rate of formation.

3.3. Ionisation Constant

The electrolytic dissociation of substances in solution is a reversible process. If we apply the law of mass action to the dissociation of a compound K_nA_m in solution into ions K^{m+} and A^{n-}

$$K_nA_m \text{ (sol)} \rightleftharpoons nK^{m+} \text{ (sol)} + mA^{n-} \text{ (sol)}$$

we obtain

$$K = \frac{[K^{m+}]^n [A^{n-}]^m}{[K_nA_m]}$$

In this case the equilibrium constant characterises ionisation of a substance in solution and is therefore called the *ionisation constant*. The higher the value of the ionisation constant, obviously, the more a compound will be ionised. Since the equilibrium constant does not depend on concentration, the ionisation constant provides a more general characteristic of the strength of an electrolyte than its degree of ionisation.

That, however, holds only for weak electrolytes whose solutions contain comparatively few ions. In strong electrolytes, on the contrary, because of the large number of ions, the electrostatic interaction of the latter begins to be significant, so that they cannot behave independently of one another. The properties of strong electrolytes are such that the concentration of their ions seems to be different than it is. This results in a deviation from the law of mass action and a change in the value of K when the concentration of the solute is altered (in particular when the solution is diluted).

To extend the law of mass action to strong electrolytes, we have to take their *effective* concentration (i.e. the concentration manifesting itself in action), known as *activity* a, in the expression of the equilibrium constant, instead of their concentration. For a strong electrolyte K_nA_m

$$K = \frac{a^n_{K^{m+}} a^m_{A^{n-}}}{a_{K_nA_m}}$$

Activity (like concentration) is expressed in mol/litre. The relationship between activity a and concentration c is expressed by the equation $a = fc$, where f is the *activity coefficient* characterising the difference between the properties of solutions of strong electrolytes and dilute solutions of weak electrolytes. In dilute solutions (close to ideal) there is practically no electrostatic interaction of the ions because they are a considerable distance apart from one another. In this case the activity coefficient is close to unity, i.e. $a \cong c$. Activity and the activity coefficient are determined from experimental findings.

In discussing the following material we shall take it that the concentration of dilute solutions of electrolytes does not differ significantly from their activity.

Ionisation constants of acids and bases. Let us apply the law of mass action to the ionisation of acids in aqueous solutions. For example, the ionisation constant for acetic acid

$$CH_3COOH + H_2O \rightleftarrows OH_3^+ + CH_3COO^-$$

will be

$$K = \frac{[OH_3^+][CH_3COO^-]}{[CH_3COOH][H_2O]}$$

The concentration of water H_2O in dilute solutions is practically constant; it is therefore advisable to include its value in the equilibrium constant $K[H_2O] = K_a$. The equilibrium constant K_a is called the *acid ionisation constant*:

$$K_a = \frac{[OH_3^+][CH_3COO^-]}{[CH_3COOH]}$$

or, simplified

$$CH_3COOH \rightleftarrows H^+ + CH_3COO^-$$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.75 \times 10^{-5}, \quad pK_a = 4.75$$

The acid ionisation constant can be determined experimentally by measuring the electrical conductivity of a solution.

The stronger the acid, the greater, obviously, its ionisation constant (Table 21). The numerical value of K_a is often replaced by its negative decimal logarithm and designated as pK_a, in order to characterise the strength of acids:

$$pK_a = -\log K_a$$

The values of pK_a for weak acids are positive. The weaker an acid, the higher the value of pK_a. Its values are negative for strong acids (see Table 21).

Table 21. Classification of Oxyacids by Strength in Aqueous Solution

Type of acid	Acid	K_a	pK_a	Acid strength
$E(OH)_n$	HBrO	2.06×10^{-9}	8.7	Very weak
	HClO	3.2×10^{-8}	7.5	
	HIO	2.3×10^{-11}	10.64	
	H_3AsO_3	6×10^{-10}	9.2	
	H_3BO_3	5.8×10^{-10}	9.24	
	H_4SiO_4	2×10^{-10}	9.7	
	H_6TeO_6	2.0×10^{-8}	7.7	
$EO(OH)_n$	$HClO_2$	1.1×10^{-2}	1.97	Weak
	HNO_2	4×10^{-4}	3.4	
	H_2CO_3	1.32×10^{-4}	3.88	
	H_2SO_3	1.3×10^{-2}	1.87	
	H_3AsO_4	6.46×10^{-3}	2.19	
	H_3PO_4	7.25×10^{-3}	2.12	
	H_5IO_6	3.1×10^{-2}	1.57	
$EO_2(OH)_n$	$HBrO_3$	2×10^{-1}	0.7	Strong
	$HClO_3$		~-1	
	HIO_3	1.7×10^{-1}	0.77	
	HNO_3	4.36×10	-1.64	
	H_2MnO_4	$\sim10^{-1}$	~1	
	H_2SO_4	1×10^{3}	-3	
$EO_3(OH)_n$	$HClO_4$		~-10	Very strong
	$HMnO_4$	2×10^{2}	-2.3	

Note: The K_a value of the first degree of ionisation is used.

Polybasic acids ionise in steps, each step having its own ionisation constant K_a and pK_a, e.g.

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$$

$$K_{a1}=\frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}=7.25\times10^{-3},\quad pK_{a1}=2.12$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$$

$$K_{a2}=\frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}=6.31\times10^{-8},\quad pK_{a2}=7.20$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$

$$K_{a3}=\frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}=1.26\times10^{-12},\quad pK_{a3}=11.9$$

The first, second, and third ionisation constants of inorganic, oxygen-containing acids are in roughly the following ratio:

$1 : 10^{-5} : 10^{-10}$. The validity of this ratio for H_3PO_4 can readily be shown by comparing the values of K_{a1}, K_{a2}, and K_{a3} given above. The first ion of hydrogen is stripped off the molecule of the acid more easily than the next ones, since the negative charge of the acid residue increases. (This explains, for example, the almost complete absence of PO_4^{3-} ions in a solution of phosphoric acid.)

The strength of acids containing oxygen depends on the structure of the molecules. The general formula of oxyacids is $EO_m(OH)_n$, bearing in mind that acid molecules have H—O—E and E=O bonds. Research has shown that the strength of acids does not depend in practice on n (the number of OH groups), but increases markedly with m (the number of oxygen atoms not bound in OH groups, i.e. with E=O bonds). Acids with the formula $E(OH)_n$ are very weak (their first ionisation constants are $K_{a1} = 10^{-8}$-10^{-11}, $pK_{a1} = 7$-10). Acids with the formula $EO(OH)_n$ are weak ($K_{a1} = 10^{-2}$-10^{-4}, $pK_{a1} =$ = 1.5-4), acids with the formula $EO_2(OH)_n$ are strong, while those with the formula $EO_3(OH)_n$ are very strong (see Table 21).

The steep increase in the strength of acids with increase of m can be explained by the attraction of electron density to the E=O bond from the H—O bond.

With an increase in the degree of oxidation of the central atom E, the change in composition of the oxygen-containing acids formed corresponds to an increase in m, for example, $\overset{+4}{H_2SO_3}$ and $\overset{+6}{H_2SO_4}$; $\overset{+3}{HNO_2}$ and $\overset{+5}{HNO_3}$. The strength of an acid therefore normally increases with an increase in the degree of oxidation of the central atom, for example:

$HClO$	$HClO_2$	$HClO_3$	$HClO_4$
$Cl(OH)$	$ClO(OH)$	$ClO_2(OH)$	$ClO_3(OH)$
$pK_a = 7.50$	$pK_a = 1.97$	$pK_a = -1$	$pK_a = \sim -10$

A general pattern is displayed here: basic properties weaken and acid properties become stronger with an increase in the degree of oxidation of an element in the series of its hydroxides, e.g.:

$Mn(OH)_2$	$Mn(OH)_3$	$Mn(OH)_4$ H_4MnO_4	H_2MnO_4	$HMnO_4$
Medium strength base	Weak base	Amphoteric compound	Strong acid	Very strong acid

The strength of *bases* can be determined from the value of *basic ionisation constant* (designated K_b). Comparison of the K_b of the hydroxides LiOH ($K_b = 6.75 \times 10^{-1}$, $pK_b = 0.17$) and NaOH ($K_b = 5.9$, $pK_b = -0.77$) shows that the second is the stronger.

3.4. The Stability Constant of Complex Compounds

Complex compounds are generally ionised in solution into inner and outer spheres:

$$[Ni(NH_3)_6]Cl_2\ (c) \rightleftarrows Ni(NH_3)_6^{2+}\ (sol) + 2Cl^-\ (sol)$$

The complex ions formed may in turn be decomposed to a greater or less degree into their constituents:

$$Ni(NH_3)_6^{2+}\ (sol) \rightleftarrows Ni^{2+}\ (sol) + 6H_3N\ (sol)$$

The stability of complexes can be assessed from the law of mass action by expressing the equilibrium state through the ionisation constant, usually referred to as *instability constant*, K_{inst}

$$K_{inst} = \frac{[Ni^{2+}][H_3N]^6}{[Ni(NH_3)_6^{2+}]} = 9.8 \times 10^{-9}, \quad pK_{inst} = 8.01$$

The more stable a complex, the lower its susceptibility to decomposition and the lower its instability constant.

Another measure of a complex's stability is the equilibrium constant of its formation, called the *stability constant* (K_{st}). The stability constant is the reciprocal of the instability constant:

$$K_{st} = 1/K_{inst}$$

For the reaction of the forming of the $Ni(NH_3)_6^{2+}$ ion in solution

$$Ni^{2+}\ (sol) + 6H_3N\ (sol) \rightleftarrows Ni(NH_3)_6^{2+}\ (sol)$$

the stability constant is

$$K_{st} = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][H_3N]^6} = 1.02 \times 10^8, \quad \log K_{st} = 8.01$$

The stability constant is a measure of complexing: higher values correspond to greater concentrations of the complex in the equilibrium state.

Comparison of the stability constants of complex ions

$$\frac{Ag(NO_2)_2^-}{6.76 \times 10^2} \quad \frac{Ag(NH_3)_2^+}{1.47 \times 10^7} \quad \frac{Ag(S_2O_3)_2^{3-}}{2.88 \times 10^{13}} \quad \frac{Ag(CN)_2^-}{7.08 \times 10^{19}}$$

shows that the last complex is the most stable one in this series and the first the least stable.

The formation of complexes in solution consists in the successive incorporation of ligands into the inner sphere of the complexing agent and elimination initially of the coordination molecules of the solvent, e.g.

$$Ni(OH_2)_6^{2+} + H_3N \rightleftarrows Ni(OH_2)_5(NH_3)^{2+} + H_2O$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$Ni(OH_2)(NH_3)_5^{2+} + H_3N \rightleftarrows Ni(NH_3)_6^{2+} + H_2O$$
$$\overline{Ni(OH_2)_6^{2+} + 6H_3N \rightleftarrows Ni(NH_3)_6^{2+} + 6H_2O}$$

When a complex, on the contrary, decomposes into its components in solution, the ligands in the molecules of the solvent are replaced. The reaction of the forming and decomposition of complexes in

solution can thus be regarded as a reaction of ligand substitution. The concentration of the water hardly alters and it is therefore not included in the expression of the stability (instability) constant.

Since complexes are formed and decomposed in steps, each step has a certain value of the stability (instability) constant. The partial stability constants for the $Ni(NH_3)_6^{2+}$ ion can be written as follows:

$$Ni^{2+} + H_3N \rightleftarrows Ni(NH_3)^{2+}, \quad K_1 = \frac{[Ni(NH_3)^{2+}]}{[Ni^{2+}][H_3N]}, \quad \log K_1 = 2.67$$

$$Ni(NH_3)^{2+} + H_3N \rightleftarrows Ni(NH_3)_2^{2+}, \quad K_2 = \frac{[Ni(NH_3)_2^{2+}]}{[Ni(NH_3)^{2+}][H_3N]}, \quad \log K_2 = 2.12$$

$$Ni(NH_3)_2^{2+} + H_3N \rightleftarrows Ni(NH_3)_3^{2+}, \quad K_3 = \frac{[Ni(NH_3)_3^{2+}]}{[Ni(NH_3)_2^{2+}][H_3N]}, \quad \log K_3 = 1.61$$

$$Ni(NH_3)_3^{2+} + H_3N \rightleftarrows Ni(NH_3)_4^{2+}, \quad K_4 = \frac{[Ni(NH_3)_4^{2+}]}{[Ni(NH_3)_3^{2+}][H_3N]}, \quad \log K_4 = 1.07$$

$$Ni(NH_3)_4^{2+} + H_3N \rightleftarrows Ni(NH_3)_5^{2+}, \quad K_5 = \frac{[Ni(NH_3)_5^{2+}]}{[Ni(NH_3)_4^{2+}][H_3N]}, \quad \log K_5 = 0.63$$

$$Ni(NH_3)_5^{2+} + H_3N \rightleftarrows Ni(NH_3)_6^{2+}, \quad K_6 = \frac{[Ni(NH_3)_6^{2+}]}{[Ni(NH_3)_5^{2+}][H_3N]}, \quad \log K_6 = -0.09$$

It can easily be shown that the general stability constant K_{st} of the complex is the product of the partial constants characterising the separate stages of the complexing process: $K_{st} = K_1 K_2 K_3 \ldots \ldots K_n$.

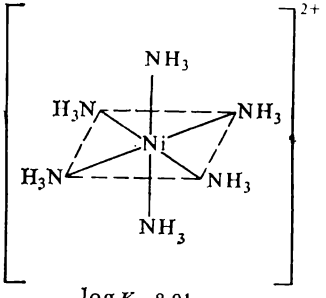
For our example it will be

$$K_{st} = K_1 K_2 K_3 K_4 K_5 K_6 = \frac{[Ni(NH_3)_6^{2+}]}{[Ni^{2+}][NH_3]^6} = 1.02 \times 10^8 \qquad \log K_{st} = 8.01$$

The example considered shows that when complex compounds are dissolved, or formed, complicated processes of ligand substitution take place in the solution.

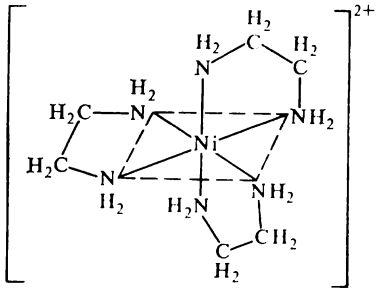
Chelate complexes are more stable than similar complexes with monodentate ligands of similar properties. For example, the nickel(II) ethylene diamine complex is about 10^9 times more stable than a similar ammoniate complex:

$[Ni(NH_3)_6]^{2+}$



$\log K_{st} = 8.01$

$[Ni(en)_3]^{2+}$



$\log K_{st} = 17.57$

For the reaction of the transition of the nonchelate complex ion $[Ni(NH_3)_6]^{2+}$ into the chelate $[Ni(en)_3]^{2+}$, the values of $\Delta H°$ and $\Delta S°$ are as follows

$$[Ni(NH_3)_6]^{2+} + 3en \rightleftarrows [Ni(en)_3]^{2+} + 6H_3N, \quad pK = 9.56$$

$$\Delta H°_{298} = -25 \text{ kJ}, \quad \Delta S°_{298} = 110 \text{ J/K}$$

In this transition the change in $\Delta H°$ is not great. At the same time, because of the increased number of dissolved particles and hence increased disorder of the system during the reaction, the entropy markedly increases. A big increase in entropy lowers the free energy significantly. The increased stability of chelate structures (compared with nonchelate ones) consequently depends primarily on the entropy factor.

3.5. Autoprotolysis Constant

Let us apply the law of mass action to the autoionisation (self-ionisation) of water

$$H_2O + H_2O \rightleftarrows OH_3^+ + OH^-$$

or

$$H_2O \rightleftarrows H^+ + OH^-$$

The ionisation constant of water

$$K_{298} = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16}$$

can be calculated, for example, from its electrical conductivity. As will be seen from the expression of the constant, water is scarcely ionised in normal conditions. Its concentration can therefore be considered constant: 55.56 mol/litre $\left(\frac{1000 \text{ g/l}}{18 \text{ g/mol}} = 55.56 \text{ mol/l}\right)$. The equation of its ionisation constant can be written as follows:

$$K [H_2O] = [H^+] [OH^-]$$

Consequently the product $K [H_2O]$ at a given temperature is also constant: $K [H_2O] = 1.8 \times 10^{-16} \times 55.56 = 10^{-14}$. Let us designate the product $K [H_2O]$ as K_w. Then $K_w = [H^+] [OH^-] = 10^{-14}$.

K_w is called the *ion product of water*. It is a constant for both pure water and dilute aqueous solutions of any substance. Its value increases with rising and decreases with falling temperature, but for calculations at room temperatures it can be taken as 10^{-14} for all cases.

The ion product of water is a very important value since it enables us to determine the concentration of H^+ (OH_3^+) in any aqueous solution, provided the OH^- concentration is known, and vice versa. The concentration of H^+ (OH_3^+) ions in pure water is equal to the concentration of OH^- ions, i.e. the medium is neutral: $[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}$ mol/l.

If the concentration of H^+ ions is higher than 10^{-7} mol/l, and the concentration of OH^- ions is less than this value, the solution will

be *acidic*. A *basic* solution, on the contrary, corresponds to a concentration of OH^- ions higher than 10^{-7} mol/l, with a concentration of H^+ ions lower than that.

The quantitative designation of a medium's reaction can be simplified if the pH value, defined as the negative logarithm of the hydrogen-ion concentration, is used: $pH = -\log_{10}[H^+]$. Then

Neutral medium	$pH = 7$
Acidic medium	$pH < 7$
Basic medium	$pH > 7$

In practice the reaction of a medium is conveniently determined by means of *indicators*, i.e. substances that change colour according to the relative concentration of H^+ and OH^- ions.

Ion products can be calculated similarly for other liquids. For ammonia at -33.4°C the ion product is

$$2H_3N \rightleftarrows NH_4^+ + NH_2^-, \quad [NH_4^+][NH_2^-] = K_S, \quad pK_S = 22$$

for sulphuric acid

$$2H_2SO_4 \rightleftarrows SO_4H_3^+ + HSO_4^-, \quad [SO_4H_3^+][HSO_4^-] = K_S, \quad pK_S = 3$$

for hydrofluoric acid

$$2HF \rightleftarrows FH_2^+ + F^-, \quad [FH_2^+][F^-] = K_S, \quad pK_S = 11.7$$

K_S is known as the *autoprotolysis constant*.

3.6. Equilibrium in Heterogeneous Systems

Equilibrium constant. Let us now consider processes involving, in addition to gaseous substances, liquid or solid reactants that do not form solid solutions with one another. The concentration of saturated vapour of a liquid or solid is constant at a given temperature. Consequently their concentrations can be included in the equilibrium constant and the expression of the law of mass action can thus be simplified. The expression of the equilibrium constant for the thermal dissociation of calcium carbonate, for instance,

$$CaCO_3\,(s) = CaO\,(s) + CO_2\,(g)$$

can be written $K = [CO_2]$ or $K_p = p_{CO_2}$. Hence it is clear that when the concentration of carbon dioxide is in equilibrium at a given temperature, the value of the constant does not depend on the quantity of $CaCO_3$ and CaO. Consequently calcium carbonate will decompose at a given temperature in a closed system until p_{CO_2} reaches a certain value, for example

Temperature, °C	762	808	870	904
p_{CO_2}, kPa	133	266	665	1065

A similar expression is obtained for the constant for all reactions in which only one component is in the gaseous state, for example,

for processes of the thermal dissociation of crystalline oxides, sulphides, hydroxides, crystal hydrates, and other compounds.

Solubility product. Let us apply the law of mass action to a heterogeneous system, i.e. a saturated solution of a barely soluble compound in equilibrium with the solid phase. If a barely soluble compound K_mA_n decomposes into K^{n+} cations and A^{m-} anions, equilibrium will be reached between the solid phase and the solution

$$K_mA_n\ (s) \rightleftarrows mK^{n+}\ (sol) + nA^{m-}\ (sol)$$

With equilibrium in a saturated solution, as many ions will pass into it in a unit of time as are precipitated from it. This equilibrium is characterised by a value known as the *solubility product* (symbol SP):

$$SP = [K^{n+}]^m [A^{m-}]^n$$

Thus, *the product of the ionic concentrations in a saturated solution of a barely soluble compound, raised to the power of the stoichiometric coefficients at a given temperature, is a constant value.**

The solubility products of certain barely soluble compounds are given in Table 22.

Table 22. **Solubility Products of Selected Barely Soluble Compounds in Water at 25 °C**

Compound	SP	pSP = −log SP	Compound	SP	pSP = −log SP
AgBr	5.3×10^{-13}	12.28	CaF_2	4.0×10^{-11}	10.40
AgCN	1.4×10^{-16}	15.84	$CaCO_3$	4.8×10^{-9}	8.32
AgCl	1.78×10^{-10}	9.75	$CaSO_4$	9.1×10^{-6}	5.04
AgI	8.3×10^{-17}	16.08	$Ca_3(PO_4)_2$	2.0×10^{-29}	28.70
$AlPO_4$	5.75×10^{-19}	18.24	CuS	6.3×10^{-36}	35.20
$BaCO_3$	5.1×10^{-9}	8.29	$Mg(OH)_2$	6.0×10^{-13}	12.6
$BaSO_4$	1.1×10^{-10}	9.97	PbS	2.5×10^{-27}	26.60

The solubility product characterises the solubility of a substance: the higher it is the greater the solubility. Thus, according to Table 22, solubility at 25°C decreases in the series AgCl—AgBr—AgI.

A saturated solution of AgCl at 25°C simultaneously contains $\sqrt{1.78 \times 10^{-10}} = 1.33 \times 10^{-5}$ mol/l Ag^+ and Cl^- ions, while a solution of AgI contains only $\sqrt{8.3 \times 10^{-17}} = 0.91 \times 10^{-9}$ mol/l of Ag^+ and I^- ions.

* Since a solution of a barely soluble compound is very dilute, the activity of the ions in solution can be taken as their concentrations.

The conditions for precipitation and dissolution of precipitates follow from the concept of solubility product. When $[K^{n+}]^m [A^{m-}]^n = SP$, the system is in equilibrium. If $[K^{n+}]^m [A^{m-}]^n > SP$, or lower than the SP, the system will tend to a new equilibrium in which the compound will be precipitated in the first case and dissolved in the second. In other words, a barely soluble electrolyte is precipitated when the product of the concentration of its ions in solution becomes *greater* than SP, e.g. in the case with AgCl when $[Ag^+] [Cl^-]$ is greater than the solubility product. This can be attained by adding excess electrolyte containing Ag^+ or Cl^- ions. The method is used to ensure complete precipitation of substances.

A precipitate dissolves when the product of the concentrations of its ions in solution is *less* than the solubility product, i.e. in our example, when $[Ag^+] [Cl^-] < SP$. This can be attained by binding either of the ions liberated in any other compound.

Instead of SP values, pSP values are often used. These are the negative logarithms of the solubility product: $pSP = -\log_{10} SP$.

CHAPTER 4

Chemical Kinetics

4.1. Velocity of Chemical Reaction

One of the basic jobs of chemistry is to establish the dependence between molecular structure, the energy characteristics of chemical bonds, and the reactivity of substances, and to study the effect of various factors on the rate and mechanism of reactions. The change in a system's free energy indicates whether a given reaction can be realised in principle, but it does not indicate whether the reaction can proceed in the given conditions, and does not provide information on the velocity and mechanism of the process. For example, the reaction between nitrogen(II) oxide and oxygen

$$2NO\ (g) + O_2\ (g) = 2NO_2\ (g), \quad \Delta G^\circ_{298} = -70\ kJ$$

proceeds very fast at room temperature, while the reaction

$$2H_2\ (g) + O_2\ (g) = 2H_2O\ (g), \quad \Delta G^\circ_{298} = -458\ kJ$$

which is characterised by a much greater reduction of free energy, will not occur in ordinary conditions. A mixture of hydrogen and oxygen can be kept for a very long time at room temperature, but at a temperature of 700°C and in the presence of a catalyst ($\Delta G^\circ_{1000} = -495$ kJ) the reaction is almost instantaneous (an explosion).

Thus, in order to describe a chemical reaction fully, it is also necessary to know the patterns that govern it in time, i.e. its rate

and detailed mechanism. The velocity and mechanism of chemical conversions are studied by the special branch of chemistry known as *chemical kinetics.*

Study of the velocities of reactions makes it possible to establish the actual mechanism of complicated chemical conversions, which in turn provides prospects of finding ways to control the chemical processes, i.e. their velocity and direction. Clarification of the kinetics of a reaction makes it possible to model the reactions taking place in chemical apparatus mathematically and to computerise the problems of optimising and automating chemical-technological processes.

Reactions may be homogeneous and heterogeneous. *Homogeneous* reactions proceed in a uniform medium (e.g. in a gaseous mixture or in a liquid solution). *Heterogeneous* reactions take place in a non-uniform medium between substances that are in different physical states (solid and liquid, gaseous and liquid, etc.). Thus, homogeneous reactions proceed uniformly throughout the entire volume filled with the reacting substances, while heterogeneous reactions proceed only at the interface of the phases. The reaction between a gaseous substance and the surface of a liquid or of a solid is an example of a heterogeneous reaction.

The *velocity of a chemical reaction* is the number of elementary events of the reaction occurring per unit of time in a unit volume (in the case of a homogeneous reaction) or per unit area of the interface (in the case of a heterogeneous reaction). It is usually characterised by the change in concentration (usually in mol/cm^3·min) of any of the reactants or products per unit of time.

The rate of a reaction can also be assessed by the rate of change of certain of the system's properties, e.g. colour, electrical conductivity, pressure, spectrum, etc.

If, at moments of time τ_1 and τ_2, the concentrations of one of the reactants are c_1 and c_2, the mean rate v in the time interval between τ_1 and τ_2 can be expressed as follows:

$$v = \frac{c_2 - c_1}{\tau_2 - \tau_1} = -\frac{\Delta c}{\Delta \tau}$$

Since the concentration of the reactants decreases, the change in the concentrations carries a minus sign.

The concentrations of the reactants are constantly changing during a chemical process, so that it is important to know the velocity of the reaction at a given moment, i.e. the *instantaneous velocity* of the reaction (ivr) which is expressed by the first derivative of the concentration as regards time

$$v = \pm \frac{dc}{d\tau}$$

If the velocity of the reaction is assessed by an increase in the concentration of one of the products, the derivative carries a plus sign.

A graph illustrating the dependence of the concentration of the reactant on time is given in Fig. 113. At each given moment of time (e.g. τ_1) the ivr is equal to the slope of the curve $v = \tan \alpha$.

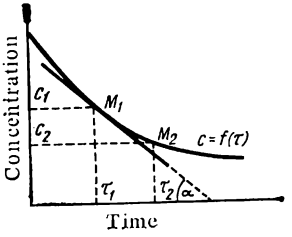


Fig. 113. Change in concentration of the initial substance during a reaction

Study of the velocities of reaction and analysis of such graphs as this provide valuable information on the mechanism of chemical reactions.

The velocity of chemical conversions depends on the *nature* and *concentration* of the reacting substances, and the *external conditions.*

The molecularity of a reaction. One, two, or three molecules may be involved in the elementary event of a reaction. Accordingly, *unimolecular*, *bimolecular*, and *termolecular* reactions are distinguished.

The probability of the simultaneous collision of a large number of particles is very small, so that even termolecular reactions are very rare, while tetramolecular reactions are not known. In most cases therefore the stoichiometric equation of a reaction does not define the character of its course, i.e. its mechanism. Most reactions consist of a series of simpler elementary stages which themselves proceed by a uni-, bi-, or termolecular mechanism.

Even reactions with relatively simple stoichiometric equations are often more complicated than one might conclude from the equation of the reaction; for example, the reaction

$$H_2\,(g) + Cl_2\,(g) = 2HCl\,(g)$$

in fact proceeds by a chain mechanism (see p. 207).

Velocity of reaction and chemical equilibrium. The velocity of a homogeneous reaction depends on the number of collisions between reacting particles in a unit volume per unit of time. The probability of their simultaneous collision, in turn, is proportional to the product of the concentrations of the reacting substances. Thus, *the velocity of a reaction is proportional to the product of reactants' concentrations.* This is one definition of the law of mass action, which was first formulated from study of dependence of the velocity of reaction on the concentration of the reactants.

For a bimolecular reaction

$$A\,(g) + B\,(g) = AB\,(g)$$

the velocity of the reaction is expressed in the form of the following kinetic equation

$$v = kC_A C_B$$

where v is the velocity of reaction, and C_A and C_B are the concentrations of the reactants A and B. The kinetic equation of a termolecular reaction

$$2A + B = AB_2$$

is

$$v = kC_A^2 C_B$$

The factor k is known as the *velocity constant*, and is equal to the velocity of the reaction when the concentration of the reactants is unity. The velocity constant of a reaction depends on the nature of the reacting substances and temperature.

Equilibrium is reached when the direct and reverse reactions proceed at the same velocity. Consider the reversible homogeneous reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$

It has been shown experimentally that the velocity of the direct reaction obeys the following kinetic equation:

$$\vec{v} = \vec{k}C_{H_2}C_{I_2}$$

and the velocity of the reverse reaction the equation

$$\overleftarrow{v} = \overleftarrow{k}C_{HI}^2$$

If H_2 and I_2 are taken as the initial substances, the velocity of the direct reaction will be determined in the first moment by their initial concentrations, while the velocity of the reverse reaction will be zero. As H_2 and I_2 are gradually used up in the reaction of forming HI, the velocity of the direct reaction will gradually decrease, while that of the reverse reaction will increase. After a certain time the velocities of both reactions will be equalised and chemical equilibrium will be established in the system, i.e. the number of HI molecules formed and decomposed per unit time will be identical.

Since the velocities of the direct and reverse reactions in equilibrium are equal ($\vec{v} = \overleftarrow{v}$),

$$\vec{k}C_{H_2}C_{I_2} = \overleftarrow{k}C_{HI}^2, \quad \text{or} \quad \vec{k}/\overleftarrow{k} = C_{HI}^2/C_{H_2}C_{I_2}$$

Since $\vec{k}$ and $\overleftarrow{k}$ are constant at a given temperature, their ratio will also be constant. Designating it as K, we get

$$K = C_{HI}^2/C_{H_2}C_{I_2}, \quad \text{or} \quad K = [HI]^2/[H_2][I_2]$$

When the conditions in which the system is in equilibrium are altered, the velocities of the two reactions will change to a different degree and the equilibrium will be upset. But after a certain time their velocities will again be equalised and chemical equilibrium restored.

4.2. Activation Energy

The velocity of most chemical reactions increases when heated. Water, for instance, cannot be synthesised from the simple substances at 20 °C since the velocity of the reaction at that temperature is so low. (It would take 54 000 million years to complete this reaction by 15 per cent at 20 °C.) But at 500 °C the reaction would take only 50 minutes, and at 700 °C the process is practically instantaneous.

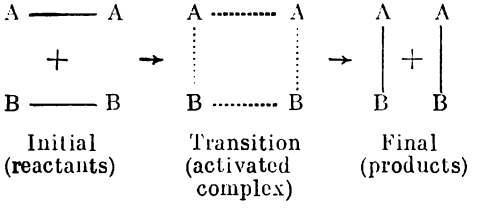
Why does heating cause such a marked acceleration of chemical conversions? To answer that we need to know what constitutes the essence of a chemical reaction. A chemical conversion takes place when the conditions are provided for a redistribution of the electron density of the colliding particles, a process that requires time and energy. There are no instantaneous processes at all in nature. A system's reactivity can be characterised by the following three consecutive states:

$$[\text{initial}] \rightarrow [\text{transition}] \rightarrow [\text{final}]$$

For the interaction of gaseous A_2 and B_2

$$A_2 + B_2 = 2AB$$

these states can be written as follows:



The intermediate state corresponds to the formation of an *activated complex* (A_2B_2). In this complex electron density is redistributed between the atoms: A—B bonds are formed simultaneously with the breaking of A—A and B—B bonds. 'Semi-destroyed' A_2 and B_2 molecules and 'half-formed' AB molecules are united, as it were, in an activated complex, which exists for a very short time only (about 10^{-13} s). Its decomposition leads to the formation of an AB molecule or of A_2 and B_2 molecules.

The formation of an activated complex requires an expenditure of energy. The probability that an activated complex will be formed when two molecules collide, and a reaction take place, depends on the energy of the colliding particles. Only those molecules will react that have sufficient energy for it. Such molecules are called *active*. The energy needed for a substance to pass into the state of an activated complex is called the *activation energy* (E_A).

The energy changes occurring in a reacting system can be shown in the form of a diagram (Fig. 114). The course of the reaction [initial state] → [transition state] → [final state] is plotted against the axis of abscissae. The potential energy of the system is plotted against the ordinate. The initial state has an energy ΣH_{in} and the final state ΣH_f. The difference in the energies of the initial and final states is equal to the heat of reaction ΔH:

$$\Delta H = \Sigma H_f - \Sigma H_{in}$$

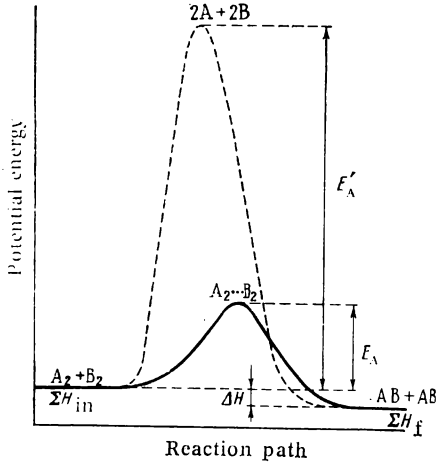


Fig. 114. Energy diagram of the $A_2 + B_2 = 2AB$ reaction

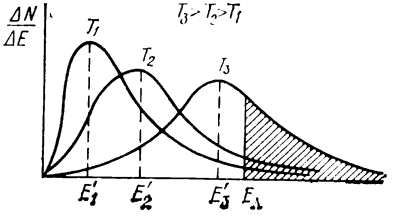


Fig. 115. Energy distribution of molecules in a system at various temperature

The energy of an activated complex is higher than that of the initial and final state of the system. Thus, the activation energy is a kind of energy barrier between the reactants and products of the reaction.

The reverse reaction (conversion of AB into gaseous A_2 and B_2), of course, proceeds through the formation of an activated complex A_2B_2, but the activation energy is different in this case from that required to synthesise AB.

As will be seen from Fig. 114 the energy expended on activating the molecules is later wholly or partly liberated during the formation of the reaction products. If the amount of energy liberated during the decomposition of an activated complex is greater than that required to activate the molecules, the reaction is exothermic and in the opposite case endothermic.

The velocity of a reaction thus depends directly on the number of molecules with sufficient energy to form an activated complex, and consequently capable of chemical conversion. The more activated molecules there are in a system, the higher the velocity of the reaction will be. One way of increasing the number of active molecules is heating. The proportion of particles possessing an energy higher than the activation energy E_A is shown in Fig. 115 (shaded part). As will

be seen from the figure, this proportion increases steeply with rising temperature ($T_3 > T_2 > T_1$). The rise in temperature in arithmetic progression usually leads to an increase in the number of active particles, and consequently of the reaction rate, in geometrical progression.

The energy barriers limit the course of the reactions so that many that are realisable in principle ($\Delta G < 0$) are therefore either retarded or do not in fact occur. Wood, paper, coal, petroleum, various fabrics, etc., can be oxidised and burn in air. The reason they do not ignite spontaneously in normal conditions (at low temperatures) is the considerable activation energy of the respective reactions.

Entropy of activation. An important condition for the occurrence of a chemical reaction, in addition to its activation energy, is the orientation of the molecules at the moment of collision. It will

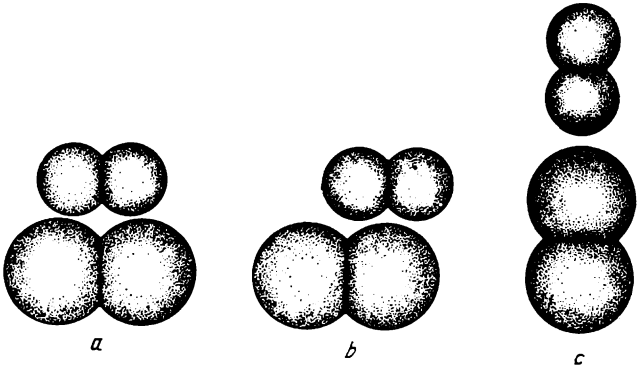


Fig. 116. Favourable (*a*) and unfavourable (*b*, *c*) orientations of A_2 and B_2 molecules when colliding

readily be appreciated that the redistribution of electron density in the activated complex $A_2 \ldots B_2$ is most favourable when the A_2 and B_2 molecules are oriented as shown in Fig. 116*a* when they collide, while the probability of a reaction is much lower when the orientation is as shown in Fig. 116*b*. The probability is even less when the orientation is as shown in Fig. 116*c*.

For a reaction to occur, the molecules must thus be oriented in a certain way when they collide and possess sufficient energy. The probability of the required orientation on collision is characterised by the *entropy of activation*, ΔS_A.

The influence of temperature. The dependence of the velocity of a chemical reaction on temperature, activation energy, and the entropy of activation is defined by the following expression for the

velocity constant of the reaction:

$$k = Ze^{-\frac{E_A}{RT}} e^{\frac{\Delta S_A}{R}}$$

where Z is the total number of collisions between molecules per second as a first approximation; T is the absolute temperature; R is the gas constant; e is the base of the natural logarithms. The probability that the colliding particles will have enough energy for their interaction is proportional to $e^{-\frac{E_A}{RT}}$. The probability of their advantageous orientation at the moment of collision is proportional to $e^{\frac{\Delta S_A}{R}}$.

It will be seen from the equation for k that since T is part of the exponent, the velocity of a chemical reaction is very sensitive to temperature changes. When, for example, the temperature is raised by 100 °C the velocity of the reaction

$$H_2\,(g) + I_2\,(g) = 2HI\,(g)$$

increases about 1000 times:

T, K	556	575	629	666	700	781
k	4.45×10^{-5}	1.37×10^{-4}	2.52×10^{-3}	1.41×10^{-2}	6.43×10^{-2}	1.34

These experimental data indicate that van't Hoff's isochore holds here: *when the temperature rises by* 10°, *the velocity of the reaction increases about two- or four-fold.* It also follows from the equation for k that the higher the activation energy, the greater the effect of temperature on the velocity of the reaction will be.

4.3. The Mechanism of Chemical Reactions

Depending on the nature of the reacting substances and the conditions of their interaction, elementary reaction events may involve atoms, molecules, radicals, or ions. Free radicals are electrically neutral particles that can be regarded as fragments of molecules e.g. $\cdot OH$ (a fragment of H_2O), $\cdot NH_2$ (a fragment of H_3N), $\cdot SH$ (a fragment of H_2S). etc. Free atoms are also classed as free radicals.

Free radicals are extremely reactive and their activation energy is very low (0-40 kJ/mol). For example, for the following reaction

$$\cdot Cl + H_2 = HCl + \cdot H, \quad E_A = 24 \text{ kJ}$$
$$\cdot H + Cl_2 = HCl + \cdot Cl, \quad E_A = 8 \text{ kJ}$$

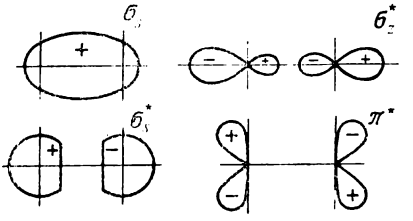
Free radicals may be formed during the decomposition of a substance by heat, light, nuclear radiation, strong mechanical action, an electric discharge, etc. They are also generated during various chemical conversions. The activation energy of reactions involving

ions is also insignificant (0-80 kJ/mol). A high activation energy is usually required for a reaction directly between molecules, so that such reactions are very rare.

For an elementary reaction event to occur, the orbitals of the interacting particles have to overlap and the conditions created for the transfer of electrons from occupied orbitals to vacant ones, i.e. the conditions in which electron density can be redistributed through the breaking of old bonds and forming of new ones.

Let us consider the mechanism of the reaction between H_2 $[(\sigma_s)^2 \times \times (\sigma_s^*)^0]$ and I_2 $[\ldots (\pi_{x,y}^*)^4, (\sigma_z^*)^0]$. We assume that the molecules H_2 and I_2 collide as shown in Fig. 116*a*, and the orbitals overlap along the x axis. This corresponds to the following combinations of orbitals

$$\sigma_s\,(H_2)—\sigma_z^*\,(I_2) \quad \text{and} \quad \sigma_s^*\,(H_2)—\pi^*\,(I_2)$$



(The shape of the orbitals is shown in Figs. 23, 27, and 28).

The combination of the occupied σ_s orbital of H_2 and free antibonding orbital σ_z^* of I_2 results in zero overlapping. This combination of orbitals does not therefore induce any chemical interaction. The combination of the free antibonding orbital σ_s^* of H_2 and the occupied antibonding π^* orbital of I_2 is not advantageous as regards energy (iodine being more electronegative than hydrogen). So, the H_2 and I_2 molecules have no orbitals that could lead to a reaction directly between them.

A detailed study of the kinetics of the reaction of iodine and hydrogen has shown (see Fig. 117) that the iodine molecule decomposes initially into atoms

$$I_2 \rightarrow I \ldots I \rightarrow I + I, \quad E_A = 150 \text{ kJ}$$

and that a termolecular reaction then occurs:

$$I + H_2 + I \rightarrow I \ldots H—H \ldots I \rightarrow HI + HI, \quad E_A = 18 \text{ kJ}$$

which ensures overlapping of the occupied σ_s orbital of H_2 and two half-filled p orbitals of two I atoms ($5p_z^1$). Since iodine is more electronegative than hydrogen, the electron density in the activated

complex I . . . H_2 . . . I is displaced from the hydrogen molecule to the iodine atoms and the H—H bond is broken.

Chain reactions. Many chemical reactions have a chain mechanism. The specific feature of chain reactions is that a single primary activation event leads to the formation of a vast number of molecules of the initial substances. Let us consider the interaction of chlorine and hydrogen as an example:

$$H_2\,(g) + Cl_2\,(g) = 2HCl\,(g)$$

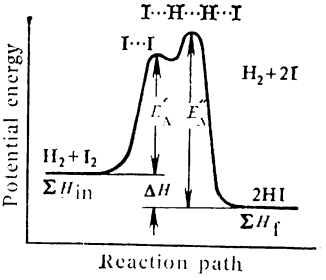


Fig. 117. Energy diagram of the H_2 (g) + I_2 (g) reaction

At normal temperatures and diffuse lighting the reaction is very slow, but if the gas mixture is heated or illuminated with light rich in ultra-violet rays (direct sunlight, the flare of burning magnesium, etc.), it explodes. Research has shown that the reaction proceeds through separate elementary processes. First the chlorine molecule absorbs a quantum of energy from the ultraviolet rays (or as a result of heating) and dissociates into free radicals (chlorine atoms)

$$Cl_2 + h\nu \rightarrow \cdot Cl + \cdot Cl$$

The valence-unsaturated ·Cl radical (atom) reacts with a molecule of hydrogen to form a molecule of HCl and an ·H atom (radical), which reacts in turn with the chlorine molecule Cl_2 to yield HCl and a ·Cl radical (atom), and so on. Thus, the reactants are converted into the product through a successive chain of elementary events, which can be represented by the following scheme:

$$\cdot Cl + H_2 \rightarrow HCl + \cdot H$$
$$\cdot H + Cl_2 \rightarrow HCl + \cdot Cl$$
$$\cdot Cl + H_2 \rightarrow HCl + \cdot H$$
$$\cdot H + Cl_2 \rightarrow HCl + \cdot Cl \text{ etc.}$$

This chain of elementary events attains a length of hundreds of thousands of links. So, when a mixture of H_2 and Cl_2 is illuminated, around 100 000 molecules of HCl are formed for each light quantum absorbed.

Free radicals can, of course, collide with one another and that would terminate the chain:

$$H\cdot + \cdot H = H_2, \quad Cl\cdot + \cdot Cl = Cl_2$$

But this only happens when the liberated energy is absorbed in a third body which happens, for example, with a triple collision

of two radicals and a molecule (M):

$$Cl\cdot + \cdot Cl + M = Cl_2 + M$$

or when energy is absorbed by the wall of the vessel. The rate of chain reactions is therefore very sensitive to extraneous matter and the shape of the vessel.

The formation of water from the simple substances

$$2H_2 + O_2 = 2H_2O$$

also has a chain character. When heat, an electric discharge, or short-wave radiation, etc., is applied, a reaction occurs between the H_2 and O_2 molecules

$$H_2 + O_2 + h\nu = \cdot OH + \cdot OH$$

The free ·OH radicals can now easily react with H_2 molecules to form a molecule of H_2O and the radical (atom) ·H:

$$\cdot OH + H_2 = H_2O + \cdot H$$

which in turn reacts with O_2 molecule to yield two radicals ·OH and ·O·:

$$\cdot H + O_2 = \cdot OH + \cdot O\cdot$$

Two radicals are also formed during the interaction of an ·O· radical (atom) with an H_2 molecule

$$\cdot O\cdot + H_2 = \cdot OH + \cdot H$$

and so on.

Each time the two last events occur, two free radicals, ·OH and ·O·, or ·OH and ·H, are produced instead of one ·H or ·O· radical. So, the number of active particles progressively increases and the velocity of the reaction is strongly accelerated. Chain reactions of this type are called *branched.*

Modern chain reaction theory owes much to the Nobel Prize winners N. N. Semyonov (USSR), C. N. Hinshelwood (Great Britain), and others.

4.4. Physical Stimulation of Chemical Conversions

Other external factors than heat, such as light, ionising radiation, pressure, mechanical action, etc., also have a substantial effect on the capacity of substances to react.

The effect of light (visible, ultraviolet) on chemical reactions is studied by a special branch of chemistry, viz., *photochemistry.* Photochemical reactions are most varied. Molecules of reacting substances are excited by absorbing quanta of light under the photochemical effect of light, i.e. become reactive or decompose into ions and free

radicals (see the synthesis of HCl above). Photochemical studies present great theoretical interest. Suffice it to say that the theory of chain reactions arose from it, and the modern concept of the mechanism of chemical reactions as a combination of elementary processes owes its development largely to it.

Photochemical processes underlie photography, i.e. the action of light on light-sensitive materials. The chain reactions of photochlorination and photosulphochlorination are widely used in industry or industrial methods of photochemically modifying polymer films and fibres. Photochemistry is directly linked with one of the most important scientific and technical problems, the utilisation of solar energy. The creation of artificial systems that could realise processes similar to photosynthesis in plants, would be of the greatest importance.

An essentially new method of affecting matter is the use of laser radiation. Its action can be both photochemical and purely thermal. Laser beams have several unique properties inherent only in this type of radiation. The most important of them for the photochemical initiation of chemical reactions is the powerful beam of luminous energy in narrow bands of the spectrum. By using radiation of a certain wavelength, therefore, which is absorbed by the reactant but does not affect admixtures it is possible to initiate a selective reaction. When a mixture of methyl alcohol, deuteromethyl alcohol, and bromine, for example, is subjected to laser radiation, only CH_3OH is brominated, and not CD_3OD, since its molecules are selectively excited and then readily react with bromine, while the CD_3OD molecules remain unexcited and do not undergo any conversions.

When a pulsed laser beam is directed onto an opaque body, the latter is heated instantaneously and evaporated; with high-power beams plasma is formed. Laser can thus be used to initiate high-temperature and plasmochemical processes, to evaporate and decompose nonvolatile substances, and so on. Laser heating of silicon and germanium, for example, in a medium of hydrogen, and of carbon in an atmosphere of chlorine, results in the formation of SiH_4, GeH_4, and CCl_4, respectively. Lasers are used to synthesise various hydrocarbons from graphite and hydrogen, reactions that cannot be realised with ordinary methods of initiation. Laser beams are now used to convert graphite into diamond, which would otherwise require high temperatures and ultrahigh pressures. These conditions can be attained by heating particles of graphite, for example, inside a massive glass block positioned at the focus of a lens condensing a laser pulse.

The use of laser radiation is exceptionally important in quantitative and qualitative analysis, and in study of the mechanisms of chemical reactions.

X-rays, gamma-rays, neutrons beams, and other high-energy radiation also cause profound physicochemical changes in matter, and initiate various reactions. Under ionising radiation, for example, oxygen forms ozone, diamond is converted into graphite, oxygen is liberated from manganese oxides, nitrogen oxides are formed from a mixture of nitrogen and oxygen (or air), SO_2 is converted in the presence of oxygen into SO_3; when water is subjected to ionising radiation *radiolysis* occurs and the water is decomposed into molecular hydrogen, oxygen, and hydrogen peroxide. The free radicals ($\cdot H$, $\cdot OH$, $\cdot HO_2$) and molecular ions ($\cdot H_2O^+$, $\cdot H_2O^-$) formed during the radiolysis of water can induce various chemical conversions of substances dissolved in water.

The chemical processes occurring through the action of ionising radiation are studied by *radiation chemistry*. Radiation-chemical reactions are now being widely used to synthesise macromolecular organic substances and to alter their structure. As atomic engineering has developed, radiation chemistry has penetrated the chemical industry more and more widely.

The chemical transformations brought about by the action of mechanical forces are studied by *mechanochemistry*. An elementary mechanochemical event is the rupture of chemical bonds in a substance under the action of mechanical forces (milling, crushing, grinding, etc.). The resultant fragments of molecules form new products; for example, during the trituration of a powder with a $V_2O_5 \times$ $\times P_2O_5 \cdot 4H_2O$ composition H_3PO_4 and $V_2O_5 \cdot H_2O$ are formed; that is to say, a kind of *mechanolysis* takes place:

$$V_2O_5 \cdot P_2O_5 \cdot 4H_2O \rightarrow 2H_3PO_4 + V_2O_5 \cdot H_2O$$

Mechanochemical transformations are being employed at present to synthesise organic polymers and alter their properties.

Even greater changes are induced in substances by ultra-high pressures. An example is the formation of denser and harder versions of a substance, as in the conversion of graphite into diamond (p. 397), or of boron nitride into borazon (p. 442), etc.

The *chemistry of shock compression* has been highly developed in recent years. Very high pressures are created in substances in a millionth of a second through the compression of solids and liquids by the shock waves generated, for example, by the detonation of explosives. Active particles of both a radical and an ionic type are thereby formed. The results of the passage of the shock wave through a substance can be most varied. On the one hand, the explosion crushes a substance into simpler constituents; on the other hand an opposite conversion is also possible, i.e. more complicated molecules and even long polymer chains may be formed from simple molecules.

Crude rubber, for example, is converted into cured rubber by a shock wave in a fraction of a second; amino acids are converted into the simplest proteins, etc.

When a shock wave passes through metals they are strongly heated and can thus be alloyed though their melting and boiling points may greatly differ, as is the case with tungsten and manganese. The former melts at 3380 °C while manganese boils at 2080 °C, and they cannot be alloyed by ordinary methods.

New ways of carrying out chemical processes in industry and methods of controlling the reactivity of substances are now being sought. In that connection the processes occurring in matter under various physical actions are therefore being very intensively studied.

4.5. Catalysis

One of the commonest methods of accelerating reactions used in chemistry is catalysis. In the presence of a catalyst the way the overall reaction proceeds is altered, and therefore its velocity as well. *Catalysts* are substances that change the rate of a chemical reaction by participating in an intermediate chemical interaction with the components of the reaction, with subsequent recovery of their own chemical composition after each cycle of the intermediate interaction. Accelerating the rate of a catalysed reaction is associated with a lower activation energy of a new path.*

The change in the velocity of a catalysed reaction through lowering the activation energy of its separate stages can be illustrated by the following example. Assume that substances A and B can react to form a compound AB ($\Delta G < 0$)

$$A + B \rightarrow \underset{\text{Activated complex}}{A \ldots B} \rightarrow AB$$

Because of its high activation energy, however, the reaction proceeds at a very slow rate (practically zero). Let us assume, on the other hand, that there is a third substance C (catalyst) which readily reacts with A to form a compound AC (because of the different nature of the reactants and consequently different, lower, activation energies):

$$A + C \rightarrow \underset{\text{Activated complex}}{A \ldots C} \rightarrow AC$$

Compound AC itself reacts readily with B (again because of the different nature of the substances and the low activation energy)

* There are also negative catalysts, substances that *slow down* the rate of a reaction. In this case the presence of the catalyst precludes realisation of the reaction through one of the pathways the reaction could follow (in the absence of the catalyst), and leaves only a slower one, so that the reaction is retarded or even completely inhibited.

to form AB and C:

$$B + AC \rightarrow \underset{\text{Activated complex}}{B \ldots AC} \rightarrow AB + C$$

Adding these last two equations we have

$$A + B = AB$$

i.e. the catalyst remains unaltered by the reaction.

The energy diagram of the reaction in the absence (curve *1*) and the presence (curve *2*) of a catalyst is shown in Fig. 118. The activation energy of the reaction evidently is lowered by ΔE_c in the presence of the catalyst.

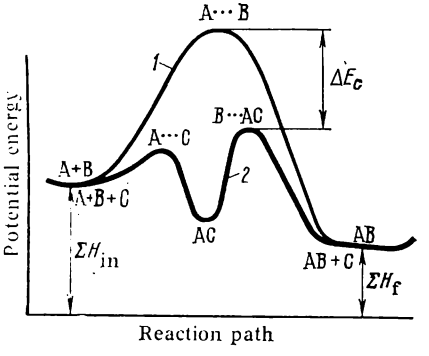


Fig. 118. Energy diagram of a reaction in the absence and presence of a catalyst

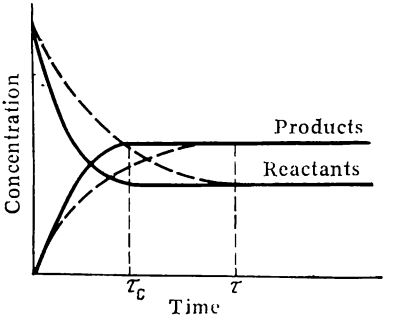


Fig. 119. Time taken to reach equilibrium in the presence and absence of a catalyst

The effect of a catalyst on lowering the activation energy of a process E_A can be illustrated by the following data for the breakdown of hydrogen iodide:

$$2HI = H_2 + I_2$$

	E_A, kJ
Without a catalyst	168
With an Au catalyst	105
With a Pt catalyst	59

Since activation energy is part of the negative exponent in the expression of the velocity constant (see p. 205), even a small reduction in it greatly accelerates the velocity of the reaction. Thus, for the reaction considered, a reduction of the activation energy by 40 kJ increases the velocity of the reaction 30 000 times over at 500 K.

In some reactions the catalyst acts as a donor of free radicals, so that the reaction begins to proceed by a chain mechanism. For instance, the oxidation of CO by oxygen

$$2CO + O_2 = 2CO_2$$

is considerably accelerated in the presence of water vapour, which is caused by the development of chains involving ·OH and ·H free radicals

$$\cdot OH + CO = CO_2 + \cdot H$$
$$\cdot H + O_2 = \cdot OH + \cdot O\cdot$$
$$CO + \cdot O\cdot = CO_2$$

Catalysts have no effect on chemical equilibrium since they equally accelerate the direct and reverse reactions. Catalysts only accelerate the establishment of equilibrium in the system. As Fig. 119 shows, equilibrium concentrations of the components in the system (τ_c) are attained in the presence of a catalyst sooner than in its absence (τ).

Catalytic reactions are most varied. In many reactions the catalytic effect is latent, which applies primarily to the reactions in solutions. As we have seen, polarisation, dissociation, and ionisation (forms of activation) occur in solutions under the action of the solvent, which in this case obviously acts as a catalyst. OH_3^+ and OH^- ions have a great effect on the velocity and direction of the processes.

Depending on the physical state of the catalyst and reacting substances, *homogeneous* and *heterogeneous* catalyses are distinguished. Examples of a homogeneous catalysis are (a) the oxidation of CO (in the gaseous state in the presence of water vapour) by oxygen and (b) the action of various enzymes in biological processes. Examples of a heterogeneous catalysis are the synthesis of ammonia over an iron catalyst, the oxidation of SO_2 to SO_3 over a platinum or vanadium oxide catalyst, etc.

CHAPTER 5

Reactions Without Change of the Elements' Oxidation State

5.1. Conditions for One-way Reactions

Reactions with or without change in the elements' oxidation state are distinguished. The division is quite arbitrary, of course, and is based solely on a formal criterion, viz., the possibility of quantitatively determining an arbitrary value, i.e. the oxidation state (or number) of an element. The invariability of elements' oxidation

state in chemical transformations by no means signifies that there is no rearrangement of the electron structures of the interacting atoms, ions, and molecules. In this case, too, the course of the reaction is always associated with a greater or less change in the character of the interatomic, interionic, and intermolecular bonds, and consequently with changes in the atoms' effective charges.

Reactions without change in the elements' oxidation state occur mostly in gaseous and liquid solutions involving ions. Ionic reactions being reversible, each system of ions corresponds in theory in given conditions to a certain equilibrium. Chemical equilibrium is displaced (sometimes more or less completely) as the concentration of some ions falls through the formation of relatively weakly ionised molecules or complex ions, barely soluble or volatile compounds (i.e. Berthollet equation). In a *neutralisation* reaction, for instance, the ionic reaction proceeds in the direction of the formation of weakly ionised molecules of the solvent, e.g. in an aqueous solution

$$\begin{array}{cccc} KOH\ (sol) + HNO_3\ (sol) = KNO_3\ (sol) + H_2O\ (l) \\ -439 \qquad -111 \qquad -393 \qquad -237 \end{array}$$

$$\Delta G_{298} = -80 \text{ kJ}$$

$$\begin{array}{cccc} RbOH\ (sol) + 1/2\ H_2SO_4\ (sol) = 1/2\ Rb_2SO_4\ (sol) + H_2O\ (l) \\ -438 \qquad 1/2\ (-745) \qquad 1/2\ (-1317) \qquad -237 \end{array}$$

$$\Delta G^\circ_{298} = -80 \text{ kJ}$$

(Standard Gibbs' energies of formation ΔG°_{298} are given below the formulas of the compounds, in kJ/mol.)

Neutralisation reactions between strong acids and alkalis proceed similarly irrespective of their nature: the change in ΔG of the reaction corresponds to one and the same process

$$\begin{array}{cccc} H^+\ (sol) + OH^-\ (sol) \rightleftharpoons H_2O\ (l), \qquad \Delta G^\circ_{298} = -80 \text{ kJ} \\ 0 \qquad -157 \qquad -237 \end{array}$$

or

$$OH_3^+\ (sol) + OH^-\ (sol) \rightleftharpoons 2H_2O\ (l)$$

In liquid ammonia this reaction corresponds to the interaction

$$NH_4^+\ (sol) + NH_2^-\ (sol) \rightleftharpoons 2H_3N\ (l)$$

A chemical reaction may also proceed through the formation of weakly ionised complex ions. $Zn(OH)_2$, for example, insoluble in water readily dissolves in the presence of ammonia with the formation of a stable cation complex $Zn(NH_3)_4^{2+}$ ($\log K_{st} = 8.7$):

$$Zn(OH)_2\ (s) + 4H_3N\ (sol) = [Zn(NH_3)_4](OH)_2\ (sol)$$

Zinc hydroxide $Zn(OH)_2$ also dissolves in an excess alkali, forming an anion complex $Zn(OH)_4^{2-}$ ($\log K_{st} = 17.70$):

$$Zn(OH)_2\ (s) + 2KOH\ (sol) = K_2[Zn(OH)_4]\ (sol)$$

When solutions of $BaCl_2$ and Na_2SO_4 are mixed together, a barely soluble compound $BaSO_4$ (pSP = 9.97) is formed:

$$BaCl_2\ (sol) + Na_2SO_4\ (sol) = 2NaCl\ (sol) + BaSO_4\ (c)$$

$$Ba^{2+}\ (sol) + SO_4^{2-}\ (sol) = BaSO_4\ (c), \quad \Delta G^\circ_{298} = -47\ kJ$$

$$-561 \qquad -745 \qquad -1353$$

A reaction proceeds by the formation of volatile compounds that escape from the reaction sphere, e.g.

$$Na_2CO_3\ (c) + 2HCl\ (sol) = 2NaCl\ (sol) + CO_2\ (g) + H_2O\ (l)$$

$$CO_3^{2-}\ (sol) + 2H^+\ (sol) = CO_2\ (g) + H_2O\ (l), \quad \Delta G^\circ_{298} = -103\ kJ$$

$$-528 \qquad 0 \qquad -394 \qquad -237$$

In contrast to these examples, the mixing of solutions of NaCl and KNO_3 does not lead to a chemical interaction:

$$NaCl\ (sol) + KNO_3\ (sol) = NaNO_3\ (sol) + KCl\ (sol)$$

$$Na^+\ (sol) + Cl^-\ (sol) + K^+\ (sol) + NO_3^-\ (sol) =$$

$$= Na^+\ (sol) + NO_3^-\ (sol) + K^+\ (sol) + Cl^-\ (sol)$$

The Na^+ and K^+, Cl^- and NO_3^- ions remain practically unchanged in solution.

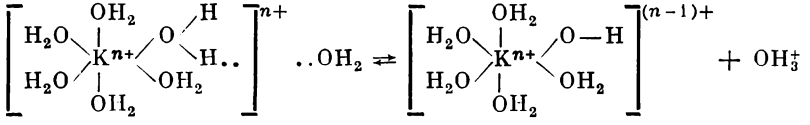
5.2. Hydrolysis

Another process that normally takes place without change in the elements' oxidation state is *hydrolysis*. In general, we understand by hydrolysis the double decomposition of water and a suitable compound. Hydrolysis is a special case of *solvolysis*, the double decomposition of a solute and solvent.

The mechanism of hydrolysis varies greatly for different types of compound. The hydrolysis of compounds dissociating in solution into ions, for example, can be regarded as the result of a polarisation interaction between the ions and their hydrate shell. The character and degree of the dissociation of the molecules of the hydrate shell depend on the nature of the cations and anions: the stronger the ions' polarising action, the more intense the hydrolysis.

In an aqueous solution, cations, it will be recalled, exist as cation aquo complexes formed by a donor-acceptor interaction ($K{-}OH_2$). Aquo complexes, in turn, are hydrated by hydrogen bonds. It can be assumed that the higher the charge and the smaller the cation, the stronger are its acceptor properties (the stronger the $K{-}OH_2$ bond), the more the O—H bond of the coordinated water molecule will be polarised, and the stronger the hydrogen bond will be between the coordinated water molecule in the complex and the water molecules of its hydrate shell. All this can lead to rupture of the O—H bond in the coordinated water molecule and to conversion of the hydrogen bond $-H \ldots OH_2$ into a covalent one with the

formation of an OH_3^+ ion and a hydroxy aquo complex:



Depending on the successive strengthening of the cations' acceptor properties (with increasing charge and diminishing size) two cases are possible:

1. The absence of noticeable decomposition of the water molecules

$$Na^+ + HOH \rightleftharpoons \text{practically no reaction}$$

(weak acceptors of electron pairs, i.e. cations of the alkali and alkaline earth metals, i.e. cations forming strong bases, alkalis, behave in this way);

2. Reversible decomposition of water molecules with the formation of hydroxy aquo complexes

$$[Al(OH_2)_6]^{3+} + HOH \rightleftharpoons [Al(OH_2)_5(OH)]^{2+} + OH_3^+$$

or

$$Al^{3+} + HOH \rightleftharpoons AlOH^{2+} + H^+$$

An excess of OH_3^+ accounts for the acidic medium of the solution. This is the commonest case and is characteristic of dipositive and tripositive ions (Cu^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}), i.e. cations forming weak bases. The weaker the base, obviously, the more intense the hydrolysis.

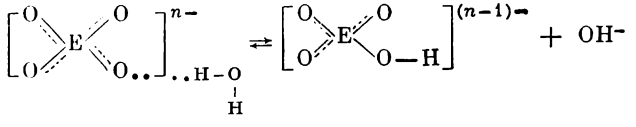
The effect of the nature of a cation (its size and charge) on the degree of ionisation of coordinated water molecules can be determined from the acid ionisation constant of the aquo complex

$$K_1 = \frac{[[M(OH_2)_5OH]^{(n-1)+}][H^+]}{[M(OH_2)_6^{n+}]}$$

which has the following values

	$[Mg(OH_2)_6]^{2+}$	$[Al(OH_2)_6]^{3+}$	$[Cr(OH_2)_6]^{3+}$	$[Fe(OH_2)_6]^{3+}$	$[Tl(OH_2)_6]^3$
pK_1	11.4	4.95	3.90	2.2	1.1

Since anions are hydrated by means of hydrogen bonds they can be converted into covalent bonds as a result of a polarisation interaction between the complexing agent (anion) and the water molecules. A proton can be split off from the water molecule and attached to the anion:



The greater the negative charge, and the smaller the anion, the more readily does the latter donate electron pairs and the more easily it extracts a proton from the water molecule. Thus, the hydroxy anions of *p* elements of period III form the following series in order of the increasing strength of the hydrogen bond: $ClO_4^- < SO_4^{2-} < PO_4^{3-} < SiO_4^{4-}$.

The following cases are possible depending on the donor activity of the anions:

1. The absence of noticeable decomposition of water molecules

$$Cl^- + HOH \rightleftharpoons \text{practically no reaction}$$

$$NO_3^- + HOH \rightleftharpoons \text{practically no reaction}$$

(weak donors of electron pairs, i.e. single-charged anions like Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, behave likewise; so, too, do SO_4^{2-}, SiF_6^{2-} and other radicals of strong acids);

2. Reversible decomposition of water molecules

$$CO_3^{2-} + HOH \rightleftharpoons HCO_3^- + OH^-$$

An excess of OH^- ions develops, i.e. the medium becomes alkaline. This case is most characteristic of donors of medium activity (doubly-charged and multiple-charged anions like CO_3^{2-}, PO_4^{3-}, SO_3^{2-}, S^{2-}, and also CN^-), i.e. the radicals of weak and moderately strong acids. Obviously, the weaker the acid is, the more intense the hydrolysis.

The total effect of hydrolysis depends on the nature of the cations and anions present in a solution.

(1) When, during ionisation, a compound forms cations and anions that weakly polarise the hydrate shell, hydrolysis does not in fact occur and the pH of the medium does not change:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

$$Na^+ + HOH \rightleftharpoons \text{practically no reaction}$$

$$Cl^- + HOH \rightleftharpoons \text{practically no reaction}$$

In this case we can say that the salts of a strong base and a strong acid do not undergo hydrolysis.

(2) When a compound forms cations (which polarise the molecules of the hydrate shell) and anions (which weakly polarise them) during ionisation, cation hydrolysis takes place, and an *acid* medium is formed:

$$CuCl_2 \rightleftharpoons Cu^{2+} + 2Cl^-$$

$$Cu^{2+} + HOH \rightleftharpoons CuOH^+ + H^+$$

$$Cl^- + HOH \rightleftharpoons \text{practically no reaction}$$

or, expressed in the molecular form

$$CuCl_2 + HOH \rightleftharpoons [CuOH]Cl + HCl$$

Generalising this example, we can conclude that the salts of weak bases and strong acids undergo cation hydrolysis.

(3) When a compound is ionised during dissolution into weakly polarising cations and into anions of medium polarising activity, *anion* hydrolysis occurs and an *alkaline* medium is formed as a result:

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$$

$$Na^+ + HOH \rightleftharpoons \text{practically no reaction}$$

$$CO_3^{2-} + HOH \rightleftharpoons HCO_3^- + OH^-$$

or, in the molecular form

$$Na_2CO_3 + HOH \rightleftharpoons NaHCO_3 + NaOH$$

In this case we can say in general that anion hydrolysis takes place in the salts of strong bases and weak acids.

(4) When a compound forms medium polarising cations and anions during ionisation, cation and anion hydrolysis occurs, usually with formation of barely soluble weak bases and weak acids

$$Al_2(CO_3)_3 + 6HOH \rightleftharpoons 2Al(OH)_3\downarrow + 3H_2CO_3$$

The character of the medium is determined here by the relative strength of the acid and base formed. This type of hydrolysis is characteristic of the salts of weak bases and weak acids.

In the second and third cases the degree of hydrolysis (the ratio of the number of hydrolysed molecules to the total number of dissolved molecules) is usually low. In a $0.1M$ solution of Na_2CO_3, for instance, it is about 2.7 per cent at 25 °C and in a $0.1M$ solution of NaCN it is about 1.5 per cent. In the fourth case hydrolysis is practically complete.

In accordance with Le Chatelier's principle, the degree of hydrolysis rises with dilution of the solution (i.e. increasing concentration of water). For example, for the reaction

$$Na_2CO_3 + HOH \rightleftharpoons NaHCO_3 + NaOH$$

at 25 °C with a salt concentration of $0.1M$, the degree of hydrolysis is 2.7 per cent, but as high as 34 per cent with a concentration of $0.001M$.

The degree of hydrolysis also increases with rising temperature.

The hydrolysis of *covalent* compounds is substantially different in character (see p. 416). Most compounds of nonmetals with nonmetals practically do not ionise in water but undergo irreversible hydrolytic decomposition:

$$SiCl_4\ (l) + 3HOH\ (l) = H_2SiO_3\ (s) + 4HCl\ (sol)$$

$$SiS_2\ (s) + 3HOH\ (l) = H_2SiO_3\ (s) + 2H_2S\ (sol)$$

These formulas are a conventional scheme of the hydrolysis. In fact it proceeds through complicated complexing processes and cation and anion polymerisation, and in most cases the mechanism is still not clear. Hydrolysis may also be accompanied by oxidation-reduction processes.

Hydrolysis plays a major role in the vital activity of living organisms. It has a substantial influence on geochemical processes. It is widely employed in the chemical industry to obtain valuable products.

The formation of polynuclear complexes during hydrolysis. The study of hydrolysis reveals that it is accompanied with complicated processes of the formation of dinuclear and polynuclear complexes in which the linking bridges may be O, OH, NH_2, NO_2, SO_4, and other atoms and their groupings. Let us consider cation hydrolysis leading to the polymerisation of complexes through OH-group bridges.

The formation of dinuclear complexes through the joining of octahedral (tetrahedral) complexes along their edges or faces, or at their apexes (see Fig. 61) can be regarded as the first stage in cation polymerisation in solutions. Schemes are given below of the formation of dinuclear complexes in which the OH-groups act as bridges:

For M^{2+} cation complexes

$$[(H_2O)_{n-1}M-OH]^+ + \left[H-\overset{H}{O}-M(OH_2)_{n-1}\right]^{2+} \rightarrow$$

$$\rightarrow \left[(H_2O)_{n-1}M-\overset{H}{O}-M(OH_2)_{n-1}\right]^{3+} + H_2O$$

or

$$MOH^+ + M^{3+} \rightarrow M_2OH^{3+}$$

For M^{3+} cation complexes

$$\left[(H_2O)_{n-2}M\begin{matrix}OH\\OH_2\end{matrix}\right]^{2+} + \left[\begin{matrix}H_2O\\HO\end{matrix}M(OH_2)_{n-2}\right]^{2+} \rightarrow$$

$$\rightarrow \left[(H_2O)_{n-2}M\begin{matrix}H\\O\\O\\H\end{matrix}M(OH_2)_{n-2}\right]^{4+} + 2H_2O$$

or

$$M(OH)^{2+} + M(OH)^{2+} \rightarrow M_2(OH)_2^{4+}$$

For M^{4+} cation complexes

$$\left[(H_2O)_{n-3}M\begin{matrix}OH\\-OH_2\\OH\end{matrix}\right]^{2+} \quad \left[\begin{matrix}H_2O\\HO-M(OH_2)_{n-3}\\H_2O\end{matrix}\right]^{3+} \rightarrow$$

$$\rightarrow \left[(H_2O)_{n-3}M\begin{matrix}H\\O\\H\\O\\H\end{matrix}M(OH_2)_{n-3}\right]^{5+} + 3H_2O$$

or

$$M(OH)_2^{2+} + M(OH)^{3+} \rightarrow M_2(OH)_3^{5+}$$

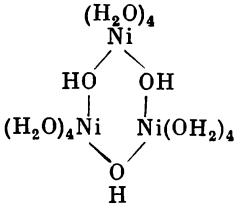
In these examples dimerisation takes place through the interaction of an OH group of one complex and a water molecule of the other, with formation of an H_2O molecule and an OH bridge.

The number of OH bridges in a dimer depends on the strength of the O—H bond in the coordinated water molecules. The higher the charge on the metal ion, the stronger is the M—O bond and the weaker the O—H bond in the coordinated water molecule, which leads to an increase in the number of OH bridges and degree of hydrolysis. The most typical forms of dinuclear complexes (according to the charge of the complexing agent) are given in Table 23.

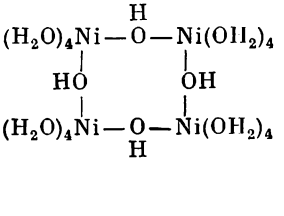
Table 23. **Forms of Dinuclear Hydroxyl Aquo Complexes**

Metal ion	Complex	Examples
M^{2+}	$M_2(OH)^{3+}$	Cu_2OH^{3+}, Be_2OH^{3+}, Zn_2OH^{3+}, Cd_2OH^{3+}, Hg_2OH^{3+}, Ni_2OH^{3+}, Pb_2OH^{3+}
M^{3+}	$M_2(OH)_2^{4+}$	$Al_2(OH)_2^{4+}$, $In_2(OH)_2^{4+}$, $Sc_2(OH)_2^{4+}$, $V_2(OH)_2^{4+}$, $Cr_2(OH)_2^{4+}$, $Fe_2(OH)_2^{4+}$, $Co_2(OH)_2^{4+}$
M^{4+}	$M_2(OH)_3^{5+}$	$Th_2(OH)_3^{5+}$, $Ce_2(OH)_3^{5+}$

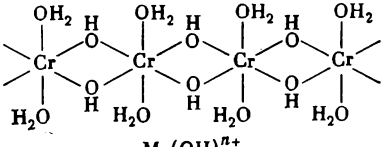
The formation of polynuclear hydroxyl aquo complexes like $M_3(OH)_3^{3+}$, $M_4(OH)_4^{4+}$, $M_n(OH)_{2n}^{n+}$ can be treated in the same way:



$M_3(OH)_3^{3+}$

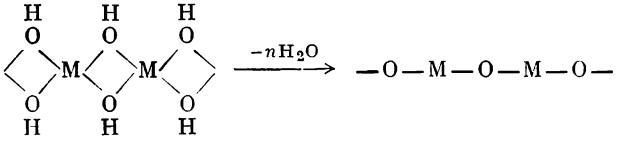


$M_4(OH)_4^{4+}$



$M_n(OH)_{2n}^{n+}$

In certain conditions (high temperature or increased pH of the solution), polycondensation may lead to the conversion of *-ol* derivatives (OH bridges) into *oxols* (oxygen bridges):



up to the formation of free oxides.

CHAPTER 6

Reactions with Alteration of Oxidation State

6.1. Oxidation-reduction Reactions

The oxidation state of elements changes during oxidation-reduction or redox reactions, which are characterised by electrons' being transferred from one particle to another. During displacement of copper by zinc from a solution of $CuSO_4$, for example,

$$CuSO_4\ (sol) + Zn\ (c) = Cu\ (c) + ZnSO_4\ (sol), \quad \Delta G^\circ_{298} = -212\ kJ$$

electrons are transferred from the zinc atoms to the copper ions:

$$Cu^{2+}\ (sol) + Zn\ (c) = Cu\ (c) + Zn^{2+}\ (sol)$$

The process by which a particle loses electrons is called *oxidation*, while the process in which electrons are gained is called *reduction*. The two processes occur simultaneously, one group of particles being oxidised and the other reduced. Hence the redox reaction is a unity of two opposite tendencies. The substances that gain electrons are called *oxidising agents* (oxidisers, or oxidants) while the substances that lose electrons are called *reducing agents* (reducers, or reductants). In the example above, Cu^{2+} is the oxidising agent and Zn the reducing agent:

$$Cu^{2+} + 2e^- = Cu, \quad Zn - 2e^- = Zn^{2+}$$

6.2. Balancing the Equations of Redox Reactions

Two methods of writing the equations of redox reaction are employed: (a) the *electronic balance* (or *oxidation-number*) and (b) the *ion-electron* (or *half-reaction*) methods. Both are actually based on the same principle: *in oxidation-reduction processes the total number of electrons donated by the reducing agent is equal to the total number gained by the oxidising agent.*

By regarding redox reactions as a simple transfer of electrons, we simplify the matter. In most cases we are simply employing a convenient way of making it easier to write the equations and choosing the coefficients for them.

Electronic balance (oxidation-number) method. In this method the number of electrons lost and gained in the reaction is calculated from the elements' oxidation numbers before and after the reaction. Let us take the following redox reaction as an example:

$$\overset{+7}{K}\overset{}{Mn}O_4 + \overset{+2}{Fe}SO_4 + H_2SO_4 \rightarrow \overset{+2}{Mn}SO_4 + \overset{+3}{Fe}_2(SO_4)_3 + K_2SO_4 + H_2O$$

The oxidation states of the elements in these compounds are changed only in the case of manganese and iron:

$$\begin{array}{l|l} \overset{+7}{Mn} + 5e^- = \overset{+2}{Mn} & 1 \\ \overset{+2}{Fe} - 1e^- = \overset{+3}{Fe} & 5 \end{array}$$

The transition of Mn(VII) to Mn(II) formally corresponds to a gain of five moles of electrons, and the transition of Fe(II) to Fe(III) to a loss of one mole of electrons. Hence, $KMnO_4$ is the oxidising agent and $FeSO_4$ the reducing agent. As the electronic balance shows, five moles of Fe(II) atoms are required for one mole of Mn(VII) atoms:

$$\overset{+7}{Mn} + 5\overset{+2}{Fe} = \overset{+2}{Mn} + 5\overset{+3}{Fe}$$

The main coefficients of the equation (the coefficients of the oxidising and reducing agents) are thus one and five respectively. It should be remembered, however, that $Fe_2(SO_4)_3$, which contains two moles of Fe(III) atoms, is formed as a result, so that the main coefficients should be doubled

$$\begin{array}{l|c|c} \overset{+7}{Mn} + 5e^- = \overset{+2}{Mn} & 1 & 2 \\ \overset{+2}{Fe} - 1e^- = \overset{+3}{Fe} & 5 & 10 \\ \hline 2\overset{+7}{Mn} + 10\overset{+2}{Fe} = 2\overset{+2}{Mn} + 10\overset{+3}{Fe} & & \end{array}$$

The coefficients found are then written into the equation:

$$2\overset{+7}{K}\overset{}{Mn}O_4 + 10\overset{+2}{Fe}SO_4 + H_2SO_4 \rightarrow 2\overset{+2}{Mn}SO_4 + 5\overset{+3}{Fe}_2(SO_4)_3 + K_2SO_4 + H_2O$$

The remaining coefficients can be found by calculating the balance of the other elements (omitting H and O), in this case K and S:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

The number of water molecules is then determined from the balance of the hydrogen atoms:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

The correctness of the equation and the coefficients selected can be checked by calculating the oxygen balance.

Since this reaction takes place in an aqueous solution, it can be represented as an ionic equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

When more than two elements change their oxidation state in a reaction, it is necessary first to establish the total number of electrons lost by the reducing agents and the number gained by the oxidising agents. The subsequent procedure is the same. For example

$$\overset{+3\ -2}{3As_2S_3} + \overset{+5}{28HNO_3} + 4H_2O = \overset{+5}{6H_3AsO_4} + \overset{+6}{9H_2SO_4} + \overset{+2}{28NO}$$

$$\begin{array}{l|l} \left.\begin{array}{l} \overset{+3}{2As} - 4e^- = \overset{+5}{2As} \\ \overset{-2}{3S} - 24e^- = \overset{+6}{3S} \end{array}\right\} 28e^- & 3 \\ \overset{+5}{N} + 3e^- = \overset{+2}{N} & 28 \end{array}$$

$$\overset{+3}{6As} + \overset{-2}{9S} + \overset{+5}{28N} = \overset{+5}{6As} + \overset{+6}{9S} + \overset{+2}{28N}$$

Sometimes the compound involved in a reaction not only acts as a reducing or oxidising agents, but also binds the reaction products (without the oxidation state of the elements being changed). For example, when a very dilute nitric acid is reduced with zinc powder

$$\overset{0}{4Zn} + \overset{+5}{HNO_3} + 9HNO_3 = \overset{+2}{4Zn}(NO_3)_2 + \overset{-3}{NH_4NO_3} + 3H_2O$$

$$\begin{array}{l|l} \overset{0}{Zn} - 2e^- = \overset{+2}{Zn} & 4 \\ \overset{+5}{N} + 8e^- = \overset{-3}{N} & 1 \end{array}$$

$$\overset{0}{4Zn} + \overset{+5}{N} = \overset{+2}{4Zn} + \overset{-3}{N}$$

one mole of the acid (out of the ten taken for the reaction) is used to oxidise the zinc while the other nine moles are used to bind the products formed by the reaction between ions of zinc and ammonium.

The reaction between manganese(IV) oxide and concentrated hydrochloric acid is an example of one in which the reducing agent also acts as a medium:

$$\overset{+4}{MnO_2} + 2\overset{-1}{HCl} + 2HCl = \overset{+2}{MnCl_2} + \overset{0}{Cl_2} + 2H_2O$$

$$\begin{array}{l|l} \overset{+4}{Mn} + 2e^- = \overset{+2}{Mn} & 1 \\ \overset{-1}{2Cl} - 2e^- = \overset{0}{Cl_2} & 1 \end{array}$$

$$\overset{+4}{Mn} + \overset{-1}{2Cl} = \overset{+2}{Mn} + \overset{0}{Cl_2}$$

The ion-electron (half-reaction) method. This method of writing oxidation-reduction equations is used for ionic redox processes and is based on deriving partial equations of half-reactions in which the ion (molecule) of the oxidising agent is reduced and the ion (molecule) of the reducing agent oxidised, with subsequent summation in the overall equation. For that purpose, an ionic scheme of the reaction has to be compiled. The ions that are not altered in the reaction are not included in the ionic scheme.

Let us return to an example considered above:

$$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$$

The ionic scheme of this reaction is

$$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$$

The Fe^{2+} ion is oxidised to Fe^{3+} while the MnO_4^- ion is reduced to Mn^{2+}. The partial half-reaction of the oxidation of the reducing ion is

$$\underset{\text{Reduced form}}{Fe^{2+}} - 1e^- = \underset{\text{Oxidised form}}{Fe^{3+}}$$

In the half-reaction equation for reduction of the oxidant ion MnO_4^- to the reduced form Mn^{2+}, it is necessary in order to balance the atoms, to add hydrogen ions so as to bind the oxygen atoms and the water. Five moles of electrons must be added to the left-hand side of the equation in order to balance the charges. The partial equation for the reduction of the oxidant ion is

$$\underset{\text{Oxidised form}}{MnO_4^-} + 8H^+ + 5e^- = \underset{\text{Reduced form}}{Mn^{2+}} + 4H_2O$$

To derive the total equation of the reaction, the partial equations must be multiplied by coefficients so that the number of moles of electrons lost will equal the number of moles of electrons gained:

$$\begin{array}{l|l} Fe^{2+} - 1e^- = Fe^{3+} & 5 \\ MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O & 1 \end{array}$$

The correctness of the equation obtained can be checked by considering the balance of the atoms and charges in the total equation:

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

When sulphuric acid is used as the medium, the molecular form of the reaction equation will be as follows:

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 2MnSO_4 + 5Fe_2(SO_4)_3 + K_2SO_4 + 8H_2O$$

Types of redox reaction. Three types of oxidation-reduction reactions are distinguished:

1. Reactions in which the oxidation state of the atoms of the elements in the various substances are changed (it will readily be noticed that the redox reactions above are of this type);

2. Reactions of oxidation-reduction decomposition of substances in which the oxidation states of the different elements in one and the same substance are changed; an example is the thermal decomposition of compounds, e.g.

$$\overset{+5\,-2}{2KClO_3} = \overset{-1}{2KCl} + \overset{0}{3O_2}$$

$$\begin{array}{l|l} \overset{+5}{Cl} + 6e^- = \overset{-1}{Cl} & 2 \\ \overset{-2}{2O} - 4e^- = \overset{0}{O_2} & 3 \end{array}$$

$$\overset{+5\quad -2}{2Cl} + \overset{-1\quad 0}{6O} = \overset{-1}{2Cl} + \overset{0}{3O_2}$$

3. Auto-redox reactions, in which the oxidation state of one and the same element is both increased and decreased. These are *disproportionation* reactions; an example is the reaction between chlorine and an alkali:

$$\overset{0}{2Cl_2} + 6KOH = \overset{-1}{5KCl} + \overset{+5}{KClO_3} + 3H_2O$$

$$\begin{array}{l|l} \overset{0}{Cl} - 5e^- = \overset{+5}{Cl} & 1 \\ \overset{0}{Cl} + 1e^- = \overset{-1}{Cl} & 5 \end{array}$$

$$\overset{0}{3Cl_2} = \overset{+5}{Cl} + \overset{-1}{5Cl}$$

In this reaction chlorine acts as both oxidant and reductant.

6.3. Direction of Redox Reactions

The direction of redox reactions can be determined by the change in the system's free energy. Furthermore, *electrode* or *oxidation-reduction potentials* E are used as a quantitative characteristic of oxidation-reduction activity of substances in solutions (or in contact with solutions).

Oxidation-reduction potentials. The relationship between ΔG and E is expressed by the following equation*

$$-\Delta G = nFE$$

where F is the Faraday number and n is the number of moles of electrons transferred in the reaction.

Electrode potentials arise as follows. If a metal plate M is immersed in a solution containing its ions

$$M^{n+}\ (sol) + ne^- \rightleftarrows M\ (c)$$

a difference of potentials, known as the *electrode potential* develops between the metal and the solution, a difference that depends on the

* $-\Delta G$ (J) = 96 495 nE (V).

nature of the metal, the concentration (or rather activity) of the ions in the solution, and the temperature.

Standard electrode potential. For a reaction occurring in standard conditions, the relation between the Gibbs' free energy and electrode potential is expressed by the equation

$$-\Delta G^\circ = nFE^\circ$$

E° is known as the *standard electrode or oxidation-reduction potential.* Its values (like ΔG°) for dissolved substances are usually taken for one mole solutions, and at 101 325 Pa for gaseous substances (see p. 182). A temperature of 25 °C is taken as standard.

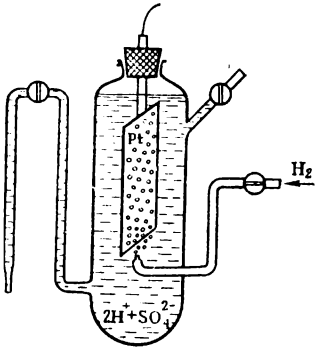


Fig. 120. A hydrogen electrode

The values of standard potentials are usually taken in relation to the system

$$H^+ \text{ (sol)} + e^- \rightleftarrows 1/2\ H_2 \text{ (g)}$$

for which the standard potential (and ΔG°) is assumed to be zero ($E^\circ = 0$). This system is called a *hydrogen electrode.*

A hydrogen electrode is a platinum plate coated with a loose layer of porous platinum (to increase the surface area of the electrode) and immersed into an aqueous solution of sulphuric acid (with a hydrogen ion activity equal to unity) (Fig. 120). Hydrogen is passed into the solution of sulphuric acid at atmospheric pressure. The part absorbed by the platinum becomes atomic hydrogen so that equilibrium is established at the surface layer of the metal

$$1/2\ H_2 \rightleftarrows H$$

while another equilibrium is established at the interface of the platinum and the solution of sulphuric acid

$$H \text{ (g)} \rightleftarrows H^+ \text{ (sol)} + e^-$$

or, to summarise

$$1/2\ H_2 \text{ (g)} \rightleftarrows H^+ \text{ (sol)} + e^-$$

The standard electrode potentials of selected oxidation-reduction systems are given in Table 24. In the series of these systems, the decreasing negative potential and increasing positive potential correspond to a drop in reducing activity and a rise in oxidising activity. For example, comparison of standard potentials of the systems

$$F_2 \text{ (g)} + 2e^- = 2F^- \text{ (sol)}, \qquad E^\circ = 2.87 \text{ V}$$
$$H_2 \text{ (g)} + 2e^- = 2H^- \text{ (sol)}, \qquad E^\circ = -2.25 \text{ V}$$

Table 24. **Standard Electrode Potentials, E°_{298}, of Selected Redox Systems in Aqueous Solutions**

Oxidised form	Number of electrons	Reduced form	E°_{298}, V
Li^+	$1e^-$	Li	−3.05
Ca^{2+}	$2e^-$	Ca	−2.87
Na^+	$1e^-$	Na	−2.71
H_2	$2e^-$	$2H^-$	−2.25
Al^{3+}	$3e^-$	Al	−1.66
Mn^{2+}	$2e^-$	Mn	−1.18
Zn^{2+}	$2e^-$	Zn	−0.76
Fe^{2+}	$2e^-$	Fe	−0.44
Cd^{2+}	$2e^-$	Cd	−0.40
Sn^{2+}	$2e^-$	Sn	−0.14
Pb^{2+}	$2e^-$	Pb	−0.13
$2H^+$	$2e^-$	H_2	0.00
$SO_4^{2-} + 2H^+$	$2e^-$	$SO_3^{2-} + H_2O$	0.22
Cu^{2+}	$2e^-$	Cu	0.34
I_2	$2e^-$	$2I^-$	0.54
Fe^{3+}	$1e^-$	Fe^{2+}	0.77
Ag^+	$1e^-$	Ag	0.80
Hg^{2+}	$2e^-$	Hg	0.85
$NO_3^- + 4H^+$	$3e^-$	$NO + 2H_2O$	0.96
Br_2	$2e^-$	$2Br^-$	1.07
$MnO_2 + 4H^+$	$2e^-$	$Mn^{2+} + 2H_2O$	1.23
$Cr_2O_7^{2-} + 14H^+$	$6e^-$	$2Cr^{3+} + 7H_2O$	1.33
Cl_2	$2e^-$	$2Cl^-$	1.36
$ClO_3^- + 6H^+$	$6e^-$	$Cl^- + 3H_2O$	1.45
$MnO_4^- + 8H^+$	$5e^-$	$Mn^{2+} + 4H_2O$	1.51
F_2	$2e^-$	$2F^-$	2.87

(Rise in reducing activity ↑ / Rise in oxidising activity ↓)

shows that the molecule F_2 has a marked oxidising tendency and the H^- ion a marked reducing tendency.

In accordance with the values of E°, zinc ($E^\circ = -0.76$ V) is a stronger reducing agent than copper ($E^\circ = +0.34$ V) and will therefore displace copper from solutions containing the Cu^{2+} ion

$$Zn\ (c) + Cu^{2+}\ (sol) = Cu\ (c) + Zn^{2+}\ (sol)$$

Chlorine ($E^\circ = +1.36$ V) is a stronger oxidising agent than bromine ($E^\circ = +1.07$ V) and will displace the latter from solutions containing Br^- ions:

$$1/2\ Cl_2\ (g) + Br^-\ (sol) = 1/2\ Br_2\ (g) + Cl^-\ (sol)$$

The direction of more complicated redox reactions can be determined from the values of oxidation-reduction potentials. For example, for the reaction

$$MnO_4^- + 5Fe^{2+} + 8H^+ = Mn^{2+} + 5Fe^{3+} + 4H_2O$$

the potentials of the half-reactions are as follows:

Oxidised form	Reduced form	Standard potential
$MnO_4^- + 8H^+ + 5e^- =$	$Mn^{2+} + 4H_2O$	1.51 V
$Fe^{3+} + 1e^- =$	Fe^{2+}	0.77 V

The standard electrode potential of the first system is higher than that of the second. Consequently, when they are in contact with each other, the first will act as an oxidising agent and the second as a reducing agent. In other words, the first reaction proceeds from left to right and the second from right to left, i.e. the Fe^{2+} ion is oxidised to Fe^{3+} and the MnO_4^- ion is reduced to Mn^{2+}.

Electrode potentials are not constant and depend on the ratio of the concentrations (or rather, activities) of the oxidised and reduced forms of the substances and on the temperature, nature of the solvent, pH of the medium, etc.

The dependence of the electrode potential on the concentration of the oxidised and reduced form and temperature is described by the Nernst equation

$$E = E^\circ + \frac{RT}{nF} \ln \frac{c_{ox}^x}{c_{red}^y}$$

or

$$E = E^\circ + \frac{2.3RT}{nF} \log \frac{c_{ox}^x}{c_{red}^y}$$

where E° is the standard electrode potential of the process; R is the universal gas constant; T is the absolute temperature; n is the number of moles of electrons transferred in an elementary process; F is the Faraday number; c_{ox} and c_{red} are the concentrations of the oxidised and reduced forms respectively (x and y are coefficients in the reaction equation).

For a temperature of 25 °C (298 K), after substituting values of constants (R = 8.31 J/mol·deg, and F = 96 500 C) the equation is transformed into

$$E = E^\circ + \frac{0.059}{n} \log \frac{c_{ox}^x}{c_{red}^y}$$

For the half-reaction

$$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$$

we can write

$$E = 1.51 + \frac{0.059}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{2+}]}$$

meaning that the concentration of water is constant, while $[MnO_4^-] = [Mn^{2+}] = [H^+] = 1$ mol/l, $E = E^\circ = 1.51$ V.

6.4. Chemical Sources of Electricity

If the process of the oxidation of the reducing agent is spatially separated from the process of the reduction of the oxidising agent an electric current can be obtained. The oxidation-reduction process will then occur at the electrodes and chemical energy will be converted directly into electricity. Any redox system can theoretically be used to obtain electricity.

Consider the following example of a redox system:

Oxidized form	Reduced form	Standard potential
$Zn^{2+} + 2e^- =$	Zn	−0.76 V
$Cu^{2+} + 2e^- =$	Cu	+0.34 V

According to the values of standard electrode potentials, the system $Cu^{2+} + 2e^- \rightleftarrows Cu$ is an oxidising agent towards the system $Zn^{2+} + 2e^- \rightleftarrows Zn$, i.e. during the contact between the two systems, the electrons will pass from Zn to Cu^{2+} ions:

$$Zn + Cu^{2+} = Zn^{2+} + Cu$$
$$\underbrace{\quad\quad}_{2e^-}$$

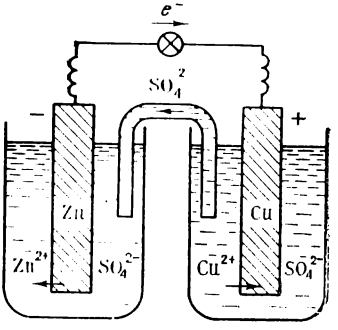


Fig. 121. Diagrammatic scheme of a voltaic cell

The reducing agent Zn can be oxidised and Cu^{2+} reduced at the electrodes of a *voltaic cell* (Fig. 121). In our case this consists of zinc and copper electrodes immersed in $ZnSO_4$ and $CuSO_4$ solutions, respectively. The vessels are connected through an U-tube filled with an electrolyte (salt bridge). When the electrodes are connected by a metallic wire, a redox reaction begins. Electrons are lost at the zinc electrode (anode) and zinc oxidised; while electrons are gained at the copper electrode (cathode) and copper ions so reduced:

anode: $Zn - 2e^- = Zn^{2+}$

cathode: $Cu^{2+} + 2e^- = Cu$

combined: $Zn + Cu^{2+} = Zn^{2+} + Cu$

$$\underbrace{\quad\quad}_{2e^-}$$

Because of the redox reaction an electric current flows in the external circuit (metal conductor) from the zinc electrode to the copper one, while SO_4^{2-} ions flow in the internal circuit (salt bridge). The zinc electrode gradually dissolves while metallic copper is deposited on the copper electrode.

The algebraic sum of the oxidation-reduction potentials of the half-reactions determines the electromotive force of the voltaic cell E_v. In our case it will be

$$E_v^\circ = E_{Cu}^\circ - E_{Zn}^\circ = 0.34 - (-0.76) = 1.1 \text{ V}$$

The direct conversion of chemical energy into electricity is one of the most pressing problems of science and engineering, and much research is currently going on into the possibility of utilising a redox reaction of burning fuel in *fuel cells*. Ordinary fuels, like coal, coke, natural gas, etc., can be employed as the oxidisable substances and oxygen or air as the oxidising agents.

As in ordinary voltaic cells, the electrodes of fuel cells, to which the reducing agent (fuel) and the oxidising agent are continuously

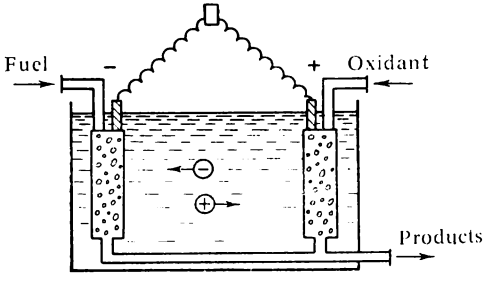


Fig. 122. Diagrammatic scheme of a fuel cell

delivered are separated by an ion-conducting electrolyte (acids and alkalis, molten salts, etc.). When gaseous products are employed the electrodes are made in the form of hollow porous tubes or plates. The current-generating process takes place at the contact surface between the electrode and electrolyte.

The operating principle of a fuel cell can be illustrated by an alkaline hydrogen-oxygen cell (Fig. 122), in which the following redox reaction is utilised:

$$2H_2\,(g) + O_2\,(g) = 2H_2O\,(l), \quad \Delta G_{298}^\circ = -474 \text{ kJ}$$

The reaction consists in the following intermediate steps: a gain of electrons at the cathode (reduction of oxygen) and a loss of electrons at the anode (oxidation of hydrogen):

cathode: $O_2 + 2H_2O + 4e^- = 4OH^-$, anode: $2H_2 + 4OH^- - 4e^- = 4H_2O$

Electrons arising at the anode move across the external circuit to the cathode, while OH^- ions move in the electrolyte from the cathode to the anode. Thus the following redox reaction takes place

$$2H_2 + O_2 = 2H_2O$$

the energy of which is not, in this case, liberated as heat but is converted directly into electricity.

The effectiveness of fuel cells is increased by using catalysts at the electrode. Platinum metals (especially palladium) are used as catalysts at the hydrogen electrode and mixed catalysts (Co and Al, or Fe, Mn, and Ag) at the oxygen electrode.

The high efficiency of fuel cells, and their continuity of operation and other advantages hold out wide prospects for their employment. They are already used in artificial Earth satellites and spacecrafts, and for military purposes. The possibility of replacing internal combustion engines by fuel cells in transport also seems very attractive.

PART TWO

SURVEY OF THE ELEMENTS AND MOST IMPORTANT CHEMICAL COMPOUNDS

> From living perception to abstract thought, *and from this to practice.*
>
> V. I. Lenin. *Philosophical Notebooks.* p. 171
>
> Only through theory does knowledge, maturing into an integral whole, become scientific knowledge; science is an ordered combination of factual knowledge and theory.
>
> A. M. Butlerov

I

INTRODUCTION TO THE CHEMISTRY OF THE ELEMENTS

CHAPTER 1

The Abundance of Chemical Elements

1.1. Geochemistry and Cosmochemistry

The average relative content of an element in any natural system (the stars, solar system, planets) is called its abundance or *clarke** (symbol C). It is usually expressed as a percentage of mass or atoms.

The chemical composition and patterns of the occurrence and distribution of elements in the Earth are studied by *geochemistry*. The subject-matter of this science was first defined by V. I. Vernadsky, who considered it the science of the history of the atoms of the Earth and a part of cosmochemistry. Its further development has been closely linked with the work of A. E. Fersman, V. M. Goldschmidt, A. P. Vinogradov, and other scientists.

The abundance and the genesis of the chemical elements in the Universe is studied by *space* or *exochemistry*. The results of geochemical studies are used to explain the information obtained on cosmic objects. Exochemistry is employed in turn to resolve problems of geochemistry.

The chemical composition of stars, planets, and nebulae is mainly studied by means of spectrographic analysis. Helium, for example,

* As suggested by A. E. Fersman, in honour of F. W. Clarke, the American geochemist who, in 1889, calculated the abundance of many elements in the Earth's crust.

was first discovered by spectrographic analysis in the Sun (1868) and only 27 years later on Earth. The composition of very distant celestial bodies is also determined by spectrum analysis.

Extremely valuable information on the physicochemical properties and composition of the atmosphere of other planets is provided by automatic space laboratories. The study of lunar soil, in particular, has been the basis of the development of *selenochemistry*.

1.2. The Abundance of Chemical Elements in the Universe

Curves of the abundance of chemical elements (for the immediate environment of the solar system) are shown in Fig. 123 in accordance with their atomic number. Their analysis shows:

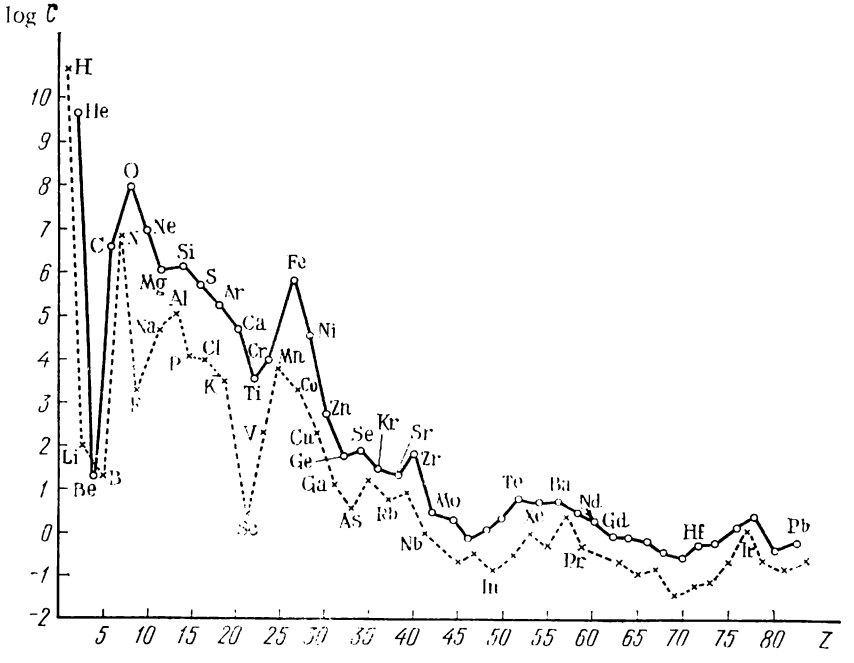


Fig. 123. The dependence of the abundance of elements in the Universe on atomic number:
data on the number of atoms are given in relation to 1×10^6 atoms of Si; the continuous curve is that of elements with an even Z and the broken line elements with an odd Z

(1) that the abundance of elements does not decrease uniformly with increasing atomic number;

(2) that the commonest elements are hydrogen and helium; three-quarters of cosmic matter consists of hydrogen and helium (by mass);

(3) that the relative abundance of atomic nuclei with an even number of protons (an even Z) is *higher* than that of nuclei with an odd number of protons (on Earth, for example, elements with an even atomic number constitute 86 per cent of the mass of the crust and those with odd number about 14 per cent);

(4) that the curves have periodically recurring peaks corresponding in the main to the magic numbers of protons and neutrons:

$$^{4}_{2}\mathrm{He}\ (2p,\ 2n),\ ^{16}_{8}\mathrm{O}\ (8p,\ 8n),\ ^{40}_{20}\mathrm{Ca}\ (20p,\ 20n),\ ^{90}_{40}\mathrm{Zr}\ (40p,\ 50n),$$

$$^{119}_{50}\mathrm{Sn}\ (50p,\ 69n),\ ^{138}_{56}\mathrm{Ba}\ (56p,\ 82n),\ ^{208}_{82}\mathrm{Pb}\ (82p,\ 126n)$$

The commonest isotope of a given element is that with an even number of neutrons; isotopes with an odd number of protons and neutrons (e.g. $^{2}_{1}\mathrm{H}$, $^{40}_{19}\mathrm{K}$) are less common.

The abundance of elements depends on many factors, but is ultimately determined by the probability of the nuclear reactions in which they are formed and the relative stability of their various isotopes. Thus, nuclei with an even number of neutrons are less liable to capture neutrons, which explains why there are more of them in nature than ones with an odd number of neutrons, which disappear through the absorption of neutrons as a result of nuclear reactions which convert them into other elements.

The comparatively low abundance of light elements like lithium, beryllium, and boron is due to their tendency to capture protons, neutrons, and other elementary particles. The low abundance of the heaviest elements is due to alpha decay and spontaneous nuclear fission.

Study of the abundance of elements throws light on the genesis and chemical history of the solar system and the Earth, and makes it possible to model the Sun and stars, to understand the physical and chemical processes taking place in outer space, and to develop theories of the formation of the elements.

1.3. Chemical Elements in the Earth's Crust

The character of the distribution of elements in the Earth's crust is about the same as their abundance in the Universe (Fig. 123). The crust contains 88 elements (Table 25). Short-lived technetium, promethium, astatine, francium, and the transuranium elements are for all intents and purposes not present in the Earth's crust, which is mainly composed of eight elements: viz., oxygen, silicon, aluminium, sodium, iron, calcium, magnesium, and potassium

(Fig. 124). These eight elements constitute about 94.5 mole per cent (mol %) or 98.5 per cent by mass (mass %) of the crust. After them come titanium, phosphorus, hydrogen, and manganese. The other elements are less than 0.6 per cent by mass.

Oxygen compounds predominate in the Earth's crust. Silicates, which are the main material of rock, are the commonest. Carbonates

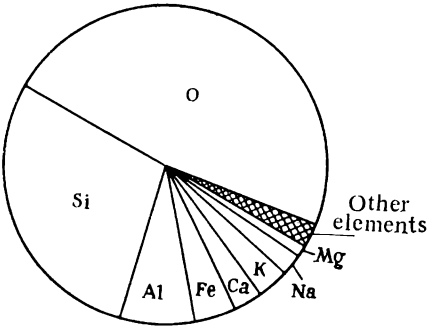


Fig. 124. **Abundance of elements in the Earth's crust (mass per cent)**

are less common, and sulphides and sulphates even less so. Some elements occur in nature as simple substances and in the native state. The forms of existence of the commonest elements on the Earth are shown in Table 26.

Depending on its chemical nature, an element may either form minerals of its own or associate with other elements. Geochemists distinguish an extensive group for which uniform distribution is characteristic and call them *scattered* or *dispersed* elements. No direct dependence has been established between the abundance of elements in the crust and the quantity of minerals formed by them. It very often happens that an element that is less abundant than another forms a larger number of minerals. Thus rubidium (0.007 mol %) has practically no minerals of its own and is a scattered element. At the same time the comparatively less abundant copper (0.0036 mol %) forms a variety of minerals and is therefore not classed as a scattered element.

Many chemical processes are constantly occurring in the crust. To understand them means to understand the mechanism by which, and the conditions in which, minerals, rocks, and ores are formed, which in turn helps us to determine the most probable location of mineral deposits.

Table 25. **Abundance of the Elements in the**

Li 6.5×10^{-3} 1.9×10^{-2}	Be 6×10^{-4} 1.2×10^{-3}							
Na 2.64 2.4	Mg 2.1 2.0							
K 2.6 1.4	Ca 3.6 2.0	Sc 6×10^{-4} 3×10^{-3}	Ti 0.65 0.25	V 1.5×10^{-2} 6×10^{-3}	Cr 2×10^{-2} 8×10^{-3}	Mn 9×10^{-2} 3.2×10^{-2}	Fe 5.1 2.0	Co 3×10^{-3} 1.5×10^{-3}
Rb 3.1×10^{-2} 7×10^{-3}	Sr 4×10^{-2} 1×10^{-2}	Y 2.8×10^{-3} 2.6×10^{-4}	Zr 2×10^{-2} 4×10^{-3}	Nb 1×10^{-3} 2×10^{-4}	Mo 3×10^{-4} 6×10^{-5}	Tc	Ru 5×10^{-7} 1×10^{-7}	Rh 1×10^{-7} 1.7×10^{-8}
Cs 7×10^{-4} 9.5×10^{-9}	Ba 5×10^{-2} 5.7×10^{-3}	La 1.8×10^{-3} 2.5×10^{-4}	Hf 3.2×10^{-4} 5×10^{-5}	Ta 2×10^{-4} 1.8×10^{-5}	W 1×10^{-4} 1×10^{-5}	Re 1×10^{-7} 8.5×10^{-9}	Os 5×10^{-6} 5×10^{-7}	Ir 1×10^{-7} 8.5×10^{-9}
Fr	Ra 1×10^{-10}	Ac 6×10^{-10} 5×10^{-15}	(Ku)	(Ns)				

Lanthanides	Ce 4.5×10^{-3} 6×10^{-4}	Pr 7.4×10^{-3} 9×10^{-5}	Nd 2.5×10^{-3} 3.5×10^{-4}	Pm	Sm 7×10^{-4} 9×10^{-5}	Eu 1.2×10^{-4} 1.8×10^{-5}
Actinides	Th 8×10^{-4} 7×10^{-5}	Pa 1×10^{-10} 8×10^{-12}	U 3×10^{-4} 2×10^{-5}	Np	Pu 1×10^{-15} 7×10^{-17}	Am

Note: The upper figure in each box indicates the mass fraction and the lower one the

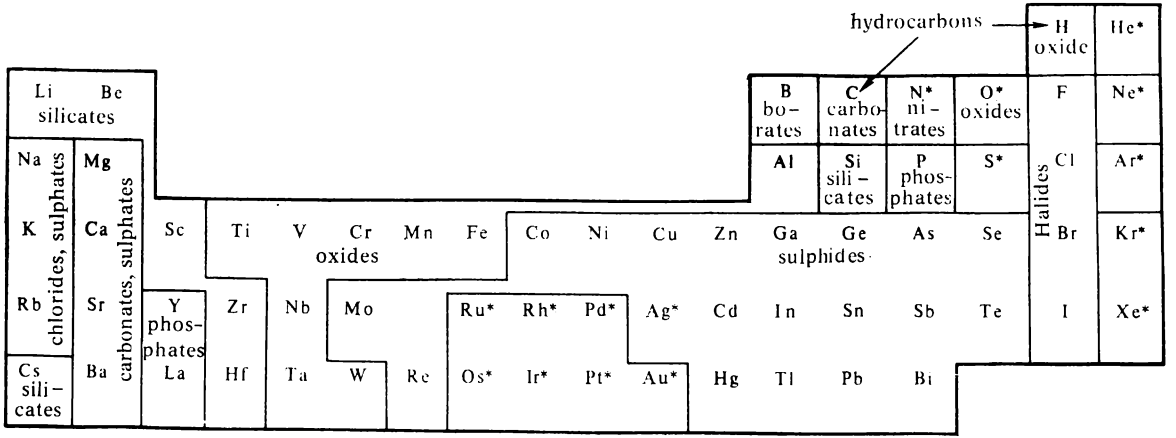
Earth's Crust (after A. P. Vinogradov)

							H 0.15 3.0	He 4.6×10^{-4}
			B 3×10^{-4} 6×10^{-4}	C 0.1 0.15	N 1×10^{-2} 2.5×10^{-2}	O 47.2 58.0	F 2.7×10^{-2} 2.8×10^{-2}	Ne 1.6×10^{-3}
			Al 8.80 6.6	Si 27.6 20.0	P 8×10^{-2} 5×10^{-2}	S 5×10^{-2} 3×10^{-2}	Cl 4.5×10^{-2} 2.6×10^{-2}	Ar 0.98 4×10^{-6}
Ni 8×10^{-3} 3.2×10^{-3}	Cu 1×10^{-2} 3.6×10^{-3}	Zn 5×10^{-3} 1.5×10^{-3}	Ga 1.5×10^{-3} 4×10^{-4}	Ge 7×10^{-4} 2×10^{-4}	As 5×10^{-4} 1.5×10^{-4}	Se 6×10^{-5} 1.5×10^{-4}	Br 1.6×10^{-4} 1.5×10^{-5}	Kr 1×10^{-4} 4×10^{-5}
Pd 1×10^{-6} 1.6×10^{-7}	Ag 1×10^{-5} 1.6×10^{-6}	Cd 5×10^{-5} 7.6×10^{-6}	In 1×10^{-5} 1.5×10^{-6}	Sn 4×10^{-3} 7×10^{-4}	Sb 4×10^{-5} 5×10^{-6}	Te 1×10^{-6} 1.3×10^{-7}	I 3×10^{-5} 4×10^{-6}	Xe 8×10^{-6}
Pt 5×10^{-7} 5×10^{-8}	Au 5×10^{-7} 5×10^{-8}	Hg 7×10^{-6} 7×10^{-7}	Tl 3×10^{-4} 3×10^{-5}	Pb 1.6×10^{-3} 1.6×10^{-4}	Bi 2×10^{-5} 1.7×10^{-6}	Po 2×10^{-14} 2×10^{-15}	At	Rn 7×10^{-16}

Gd 1×10^{-3} 1×10^{-4}	Tb 1.5×10^{-4} 1×10^{-5}	Dy 4.5×10^{-4} 5×10^{-5}	Ho 1.3×10^{-4} 5×10^{-6}	Er 4×10^{-4} 5×10^{-5}	Tm 8×10^{-5} 8×10^{-6}	Yb 3×10^{-4} 3×10^{-5}	Lu 1×10^{-4} 1×10^{-5}
Cm	Bk	Cf	Es	Fm	Md	(No)	(Lr)

mole fraction of elements.

Table 26. Forms of the Terrestrial Occurrence of the Elements



* Occur in free state.

CHAPTER 2

Simple Substances

2.1. The Structure of Simple Substances

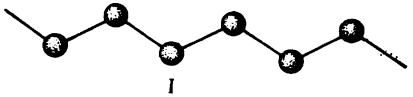
A combination of atoms of one and the same element is a *simple substance*. Depending on the type of chemical bond between the atoms, simple substances may be *metals* or *nonmetals*. A metallic bond is characteristic of metals and a covalent bond of nonmetals, but there is no sharp dividing line between metallic and nonmetallic simple substances. Metalline simple substances are classed as metals and nonmetalline ones as nonmetals.

Any one element can form various types of simple substances, known as *allotropic forms* or *allotropes*. More than 400 varieties of simple substances are now known. The phenomenon of allotropy may be due either to a different combination of molecules of the simple substance of an element (*allotropy of composition*) or to a shifting of molecules or atoms in their crystals (*allotropy of form*). The ability of an element to form corresponding allotropes depends on the structure of its atoms, which determines the type of chemical bond, and the structure of the molecules and crystals.

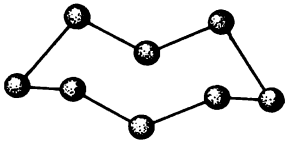
Let us consider, as an example, the types and structure of the simple substances formed by elements of the third period. In *argon* ($3s^23p^6$), the p element of group VIII having a completed valence shell ($:\ddot{\mathrm{A}}\mathrm{r}:$), the molecule is monatomic, and only a dispersion interaction is possible between its atoms. In the solid state, therefore, crystals of argon and its analogues are molecular (see Fig. 66*a*), have high coordination numbers (usually cubic face-centred or hexagonal lattices).

For *chlorine* ($3s^23p^5$), the atoms ($:\dot{\mathrm{C}}\mathrm{l}:$) can unite into molecules in one way only, by forming a diatomic covalent Cl_2 molecule with a dumb-bell shape. Chlorine crystals (like iodine crystals) are formed by molecules (see Fig. 66*b*).

As the number of unpaired electrons increases, allotropy of composition becomes possible. For *sulphur* atoms ($3s^23p^4$), which have two unpaired electrons ($\cdot\ddot{\mathrm{S}}\cdot$), unification in zig-zag chains (I) is most typical. In ordinary conditions this corresponds to a geometrical shape in the form of a zig-zag molecular chain closed in an eight-membered S_8 ring (II):



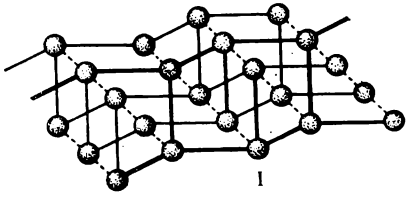
I



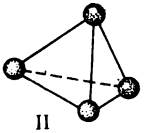
II

Apart from S_8 molecules, there are also, in the appropriate conditions, sulphur molecules in the form of open S_∞ zig-zag chains, S_6 and S_4 rings, and S_2 dumb-bell molecules.

The atoms of *phosphorus* ($3s^23p^3$), having three unpaired electrons ($\cdot\dot{\underset{\cdot\cdot}{P}}\cdot$), unite in $P_{2\infty}$ dimer layers with a pyramidal distribution of bonds (I). In addition, phosphorus atoms form P_4 tetratomic molecules of a tetrahedral configuration (II):



I



II

The most stable structure of the *silicon* atom ($3s^23p^2$) is a $Si_{3\infty}$ trimeric (coordinational) structure because of sp^3 hybridisation (see Fig. 64).

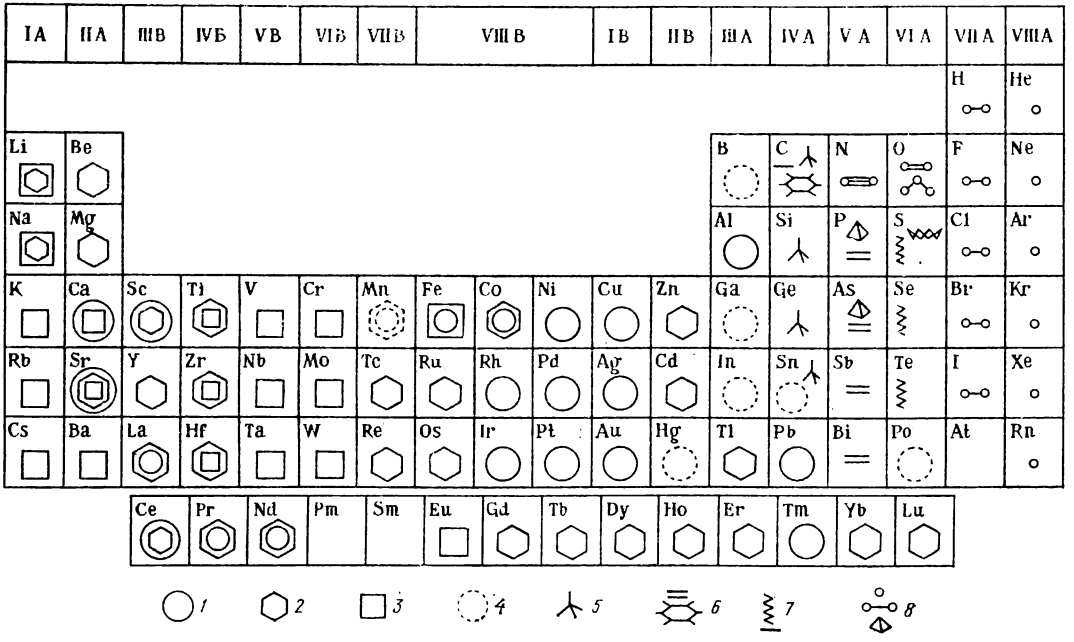
Passing from silicon to aluminium and beyond to the *s* elements magnesium and sodium, the number of valence electrons decreases and the number of free valence orbitals increases. This reduces the strength of the two-centre bond and strengthens the tendency to form nonlocalised, and finally, metallic bonds (electron gas).

Since a metallic bond is unsaturated and undirected, metals have coordination lattices with maximum close packing. As we said above (see Fig. 65) three types of lattice are most typical of simple metallic substances of the most varied chemical nature: (a) face-centred cubes (coordination number 12); (b) hexagons (coordination number 12); and (c) body-centred cubes (coordination number eight). Allotropy is characteristic of most metals. This is primarily linked with the fact that the lattice energies of various metallic structures are similar. Polymorphism occurs more often in *d* and *f* elements (especially in 5*f* ones) than in *s* and *p* elements, because of the closeness in energy of the $(n-1)$ *d* and *ns* and *np* states of *d* elements and the closeness of the 5*f*, 6*d*, and 7*s* states of 5*f* elements.

The diminishing number of valence electrons in the transition from the *p* elements of group VIII to the *s* elements of group I thus determines the regular transition from nonmetals with molecular crystal lattices (Ar, Cl_2, P_4) to nonmetals with atomic chain (S_∞), atomic layer ($P_{2\infty}$) and atomic coordination ($Si_{3\infty}$) structures, and further to metallic coordination crystals (Al, Mg, Na).

The structure of simple substances in the other periods of Mendeleev's periodic system changes in roughly the same way. A general survey of the structure of simple substances is given in Table 27.

Table 27. Structure of Simple Substances



1 – face-centred cubic, *2* — hexagonal, *3* — body-centred, *4* — other structures, *5* – diamond structure, *6* – layer lattice, *7* — chain structure, *8* — insular (molecular) structure.

2.2. Properties of Simple Substances

Physical properties. The properties of simple substances (density, melting and boiling points, electrical conductivity, etc.) alter regularly with changes in their structure and type of chemical bond. Argon, chlorine, and sulphur, for example, are dielectrics in the solid state, silicon a semiconductor, and aluminium, magnesium, and sodium metals.

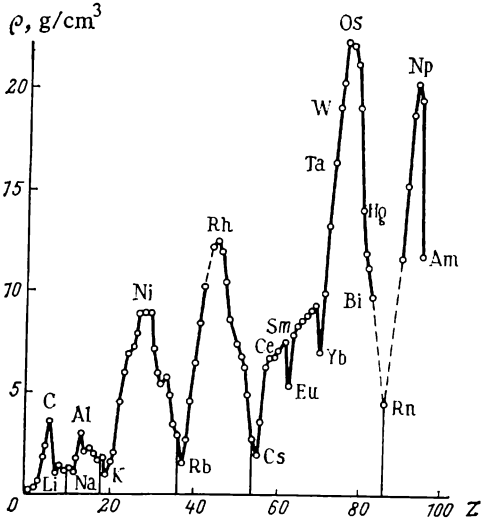


Fig. 125. Density of the simple substances

The periodic dependence of the properties of simple substances on the element's atomic number is more complicated than in free atoms, due to their not being linearly dependent on the nature of the atoms forming them but rather dependent on their structure, type of chemical bond, intermolecular interactions, formation conditions, etc.

The dependence of density of simple substances in the solid state, their melting point and standard entropy on the atomic number of the elements is shown in Figs. 125-127.

As will be seen from Fig. 126, the melting point of simple substances first increases in the periods then drops. Simple substances with a molecular structure (especially monatomic simple substances of the *s* and *p* elements of group VIII—the noble gases) have the lowest melting points. In ordinary conditions, simple substances with a molecular structure are gases, liquids, or relatively low-melting solids. Diamond and silicon, which have covalent atomic-coordination lattices, have the highest melting points.

Among metals, simple substances of *d* elements have the highest melting points. It is supposed that this is due to the covalent bond (because of *d* electrons) that is present in their crystals along with the metallic bond (through outer *s* electrons). 5*d* Electrons are highly involved in the formation of covalent bonds, so that the melting point in the subgroups of *d* elements rises with atomic number (Fig. 126).

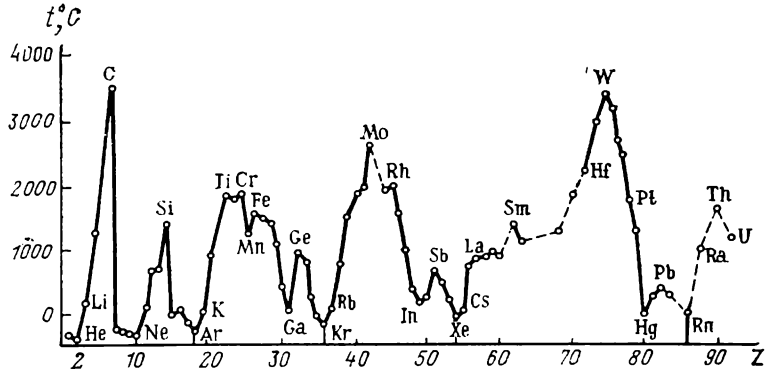


Fig. 126. Melting points of the simple substances

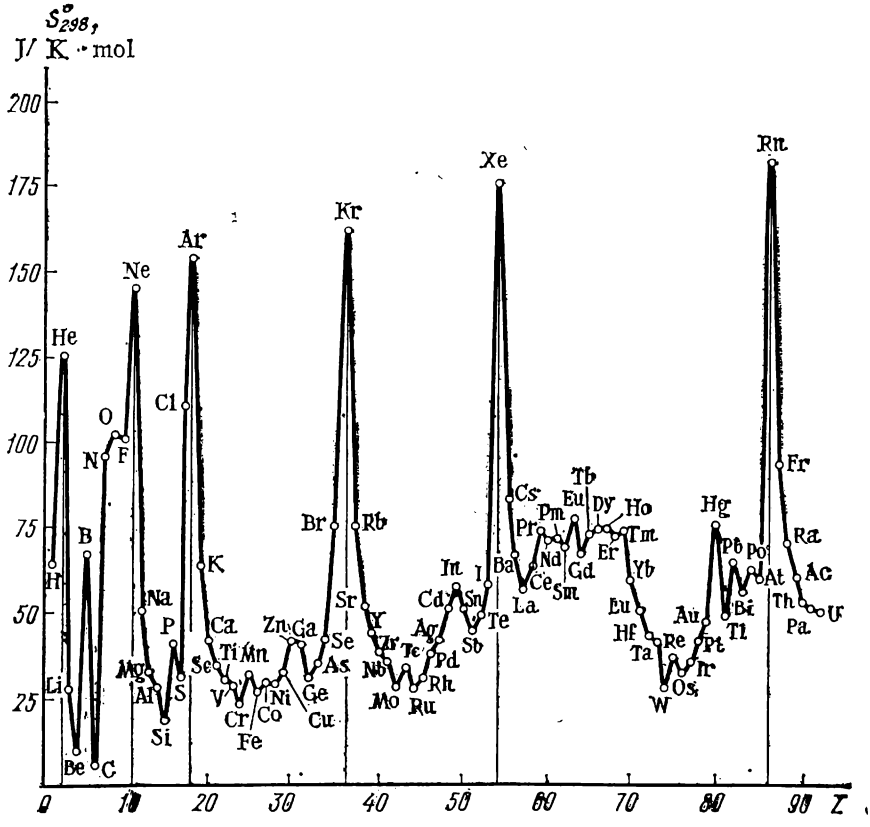


Fig. 127. Standard entropies of the simple substances

The standard entropies of simple substances (Fig. 127), unlike melting points, change in the reverse order within the period, first decreasing, then increasing. This is reflected in a gradual transition from a soft alkali metal to hard covalent polymers (diamond, silicon, germanium, antimony), and to monatomic noble gases at the end of the period.

Chemical properties of simple substances. Metals usually act as reducing agents in chemical reactions. Nonmetals, except fluorine, may display both reducing and oxidising properties, the character of the change of reducing or oxidising activity of simple substances within groups and subgroups depending mainly on the nature of the other reactants and the conditions of the reaction. There is usually a general tendency in the main subgroups: viz., for the oxidising properties of nonmetals to weaken as the atomic number of the elements increases, and for the reducing properties of metals to become stronger. This evidenced, for example, in the character of the changes in the standard Gibbs' energy of the formation of compounds of the same type. In the reaction of the oxidation of metals of the main subgroup of group II by chlorine

$$M\ (c) + Cl_2\ (g) = MCl_2\ (c)$$

the negative value of ΔG_f° increases from beryllium to barium:

	$BeCl_2$ (c)	$MgCl_2$ (c)	$CaCl_2$ (c)	$SrCl_2$ (c)	$BaCl_2$ (c)
$\Delta G_{f,\,298}^\circ$, kJ/mol	—468	—592	—750	—781	—811

In other words, the reducing activity of simple substances in respect of chlorine increases in the Be—Mg—Ca—Sr—Ba series.

When calcium is oxidised by halogens

$$Ca\ (c) + Hal_2 = CaHal_2\ (c)$$

the negative value of ΔG_f° decreases from fluorine to iodine:

	CaF_2 (c)	$CaCl_2$ (c)	$CaBr_2$ (c)	CaI_2 (c)
$\Delta G_{f,\,298}^\circ$, kJ/mol	—1162	—750	—656	—529

The oxidising activity of simple substances with respect to calcium thus decreases in the F_2—Cl_2—Br_2—I_2 series. $\Delta G_{f,298}^\circ$ for H_2O (g), H_2S (g), H_2Se (g) and H_2Te (g) are —229, —34, +20 and +85 kJ/mol respectively, which indicates a decrease in the chemical activity of the elements in the oxygen—sulphur—selenium—tellurium series as regards hydrogen.

When other substances are involved in the reaction, and the conditions of the reaction are different, the chemical activity of these simple substances may change in a different way. Lithium, for example, is the most active alkali metal in relation to fluorine (and

to oxygen):

$$M\ (c) + 1/2\ F_2\ (g) = MF\ (c)$$

	LiF (c)	NaF (c)	KF (c)	RbF (c)	CsF (c)
$\Delta G^\circ_{f,\,298}$, kJ/mol	—584	—543	—538	—523	—505

while caesium is the most active alkali metal in relation to iodine (and bromine):

$$M\ (c) + 1/2\ I_2\ (c) = MI\ (c)$$

	LiI (c)	NaI (c)	KI (c)	RbI (c)	CsI (c)
$\Delta G^\circ_{f,\,298}$, kJ/mol	—267	—285	—324	—326	—334

The change in the series of chemical activity is due to the dissimilar character of the changes in this series of elements in their

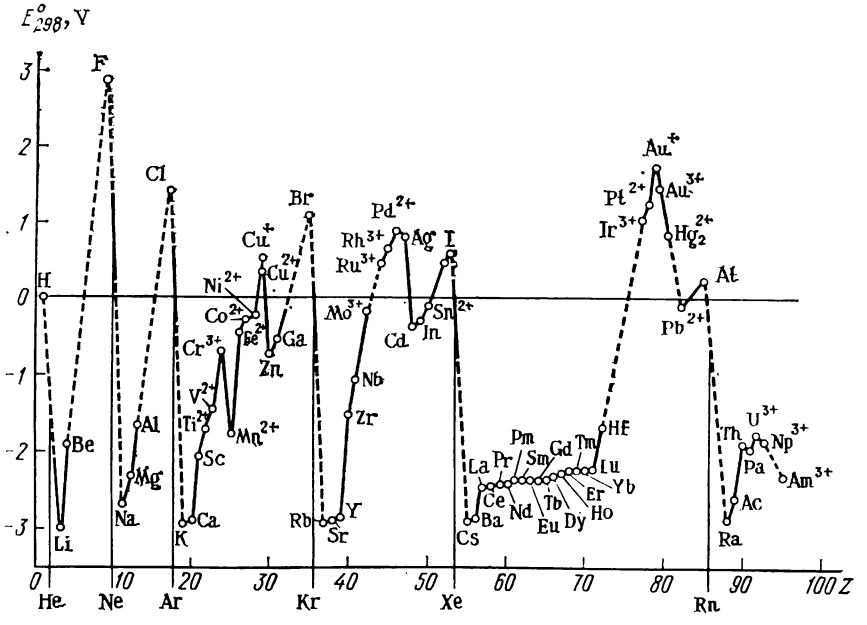


Fig. 128. Standard electrode potentials of the simple substances in aqueous solution

atomic and ionic radii, ionisation potentials, and heats of sublimation of the simple substances on the one hand, and the lattice energies of the compounds on the other.

The periodic change in simple substances' chemical activity is evidence of the character of changes in ΔH°_f and ΔG°_f of corresponding compounds of the same type with increasing atomic number of the elements. This is also indicated by Fig. 128, which shows the dependence of the standard electrode potential E°_{298} of simple substances in aqueous solution on the atomic number of the elements.

Reaction of simple substances to water. Since chemical processes often occur in aqueous media, it is very important to examine the relation of simple substances to water and aqueous solutions. The specific chemical feature of water is that it is both an oxidant and a reductant, and also acts as a ligand in the formation of complexes.

The following cases of the chemical interaction of simple substances and water are possible, depending on their nature.

1. Oxidation of the simple substance by water accompanied with liberation of hydrogen and the formation of hydrated cations. The electrode potential of the system $2H^+$ (sol) $+ 2e^- = H_2$ (g) for water (at pH 7) is $E_{298} = -0.414$ V. Hydrogen is consequently liberated in the reaction of water with metals whose electrode potential is more negative than -0.414 V, e.g.,

$$2Na\ (s) + 2HOH\ (l) = 2Na^+\ (sol) + 2OH^-\ (sol) + H_2\ (g)$$
$$2Na\ (s) + 2HOH\ (l) = 2NaOH\ (sol) + H_2\ (g)$$

This case is characteristic of the alkali and alkaline earth metals. The reaction is much faster when the hydroxide formed is soluble in water. If, however, it is insoluble, or only barely so, it forms a film on the metal and inhibits the further course of the reaction, e.g.,

$$Zn\ (s) + 2HOH\ (l) = Zn(OH)_2\ (s) + H_2\ (g)$$

The inhibition or a complete suppression of a chemical process by the reaction products is called *passivation.*

2. Disproportionation of simple substances accompanied with the formation of hydrated anions:

$$Cl_2\ (g) + 2HOH\ (l) = OH_3^+\ (sol) + Cl^-\ (sol) + HClO\ (sol)$$
$$Cl_2\ (g) + HOH\ (l) = HCl\ (sol) + HClO\ (sol)$$

This is the mechanism by which the simple substances of the most electronegative elements (Cl, Br, I) interact with water.

3. Reduction of simple substances with water accompanied with the liberation of oxygen and formation of a hydrated anion. The oxidation-reduction potential of the system

$$O_2\ (g) + 4H^+ + 4e^- = 2H_2O$$

for water (at pH 7) is $E_{298} = 0.82$ V. This is the mechanism by which fluorine, whose electrode potential is $E^\circ_{298} = 2.87$ V, interacts with water:

$$F_2\ (g) + 3H_2O\ (l) = 2OH_3^+\ (sol) + 2F^-\ (sol) + O\ (g)$$
$$F_2\ (g) + H_2O\ (l) = 2HF\ (sol) + O\ (g)$$

Substances dissolved in water may either promote display of the tendency inherent in the elements concerned to form cation or anion derivatives, or inhibit and suppress this tendency. The OH_3^+ ions, for instance, may promote the formation of cation complexes or, on

the contrary, inhibit the formation of anion complexes, while the OH^- ion prevents the formation of cation complexes and promotes the formation of anion ones. (Other negative ions, like CN^-, F^-, etc., behave likewise.)

Relation of simple substances to dilute acids. The oxidation of simple substances through the liberation of hydrogen as a rule proceeds more actively in acid solutions than in pure water. The increase in the concentration of OH_3^+ ions corresponds to a fall in the negative value of the system's electrode potential H^+ (sol) + e^- = 1/2 H_2 (g), so that the number of metals that react by this mechanism increases steeply. The presence of an excess of OH_3^+ ions, moreover, prevents the formation of hydroxides, which also promotes the passage of simple substances into cation aquo complexes:

$$Zn\ (s) + 2OH_3^+\ (sol) + 2H_2O\ (l) = [Zn(OH_2)_4]^{2+}\ (sol) + H_2\ (g)$$

or

$$Zn\ (s) + H_2SO_4\ (sol) = ZnSO_4\ (sol) + H_2\ (g)$$

In some cases, insoluble or barely soluble products are formed during the interaction of simple substances and acids, which inhibits further oxidation-reduction. Lead, for example, is insoluble in dilute acids (sulphuric acid, hydrochloric acid, etc.), since water-insoluble precipitates ($PbSO_4$, $PbCl_2$, etc.) are formed on its surface during the interaction with them and protect it against further oxidation. Insoluble products are generally formed in the interaction of metals and H_3PO_4, H_2SO_3, H_2CO_3, HF, and HCN.

Relation of simple substances to aqueous solutions of alkalis. Since OH^- ions promote the formation of anion complexes, the simple substances of elements that tend to form anion complexes can only react with aqueous solutions of alkalis; the simple substances are oxidised either by the water (with liberation of hydrogen)

$$Zn\ (s) + 2H_2O\ (l) + 2OH^-\ (sol) = [Zn(OH)_4]^{2-}\ (sol) + H_2\ (g)$$

$$Si\ (s) + H_2O\ (l) + 2OH^-\ (sol) = SiO_3^{2-}\ (sol) + 2H_2\ (g)$$

or through disproportionation:

$$Cl_2\ (g) + 2OH^-\ (sol) = Cl^-\ (sol) + ClO^-\ (sol) + H_2O\ (l)$$

These reactions proceed the more easily, of course, the more stable that complex anions are formed. Hydroxy anions of the type of $[E(OH)_n]^{x-}$ are thus most stable with Zn(II), Al(III), and Be(II) so that their simple substances are quite readily soluble in aqueous solutions of alkalis. At the same time Fe, Co, Mn and others only react with alkali solutions in the powdered state and after long heating, because of the instability of the hydroxy anions.

Relation of simple substances to aqueous solutions of oxidants stronger than OH_3^+. The tendency of elements to form cation or anion derivatives is especially clear in the oxidation of simple substances

in aqueous solutions by oxidants stronger than water or OH_3^+ ions. Nitric acid, for example, has such a strong oxidising capacity. Unlike many other acids, it oxidises not so much by its OH_3^+ ion as by the NO_3^- anion. The character of the reduction products depends on its concentration and the activity of the simple substance.

In the interaction of HNO_3 and elements with stable low oxidation states aquo complexes are formed:

$$\overset{0}{Cu} + 2\overset{+5}{NO_3^-} + 4OH_3^+ = [\overset{+2}{Cu}(OH_2)_6]^{2+} + 2\overset{+4}{NO_2}$$

$$3\overset{0}{Cu} + 2\overset{+5}{NO_3^-} + 8OH_3^+ + 6H_2O = 3[\overset{+2}{Cu}(OH_2)_6]^{2+} + 2\overset{+2}{NO}$$

or

$$Cu + 4HNO_3\ (con) = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

$$3Cu + 8HNO_3\ (dil) = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

If the HNO_3 is concentrated, NO_2 is normally liberated; when it is dilute, NO is evolved.

Elements that have characteristically high oxidation states form oxy acids when reacting with concentrated nitric acid, while the acid itself is reduced to NO:

$$\overset{0}{S} + 2\overset{+5}{HNO_3} = \overset{+6}{H_2SO_4} + 2\overset{+2}{NO}$$

$$3\overset{0}{Re} + 7\overset{+5}{HNO_3} = 3\overset{+7}{HReO_4} + 7\overset{+2}{NO} + 2H_2O$$

Concentrated sulphuric acid reacts with simple substances in the same way and is generally reduced to SO_2

$$\overset{0}{Cu} + 2\overset{+6}{H_2SO_4} = \overset{+2}{CuSO_4} + \overset{+4}{SO_2} + 2H_2O$$

$$2\overset{0}{P} + 5\overset{+6}{H_2SO_4} = 2\overset{+5}{H_3PO_4} + 5\overset{+4}{SO_2} + 2H_2O$$

2.3. Preparation of Simple Substances

The overwhelming majority of chemical elements on the Earth are found in the form of compounds. Depending on the sign of a particular element's oxidation state, its simple substance can be obtained by oxidising or reducing appropriate compounds. Oxidation is employed for simple substances whose oxidation states in compounds are negative, while reduction is used when the simple substances have positive oxidation states in compounds.

The redox processes can be realised through chemical reactions, electrochemically, or by thermal decomposition of substances.

Chemical methods of obtaining simple substances. Chemical *oxidation* of compounds is employed in industry to obtain, for example,

simple substances of such highly electronegative elements as bromine and iodine:

$$2NaBr + Cl_2 = 2NaCl + Br_2$$

In the laboratory the method is used to obtain chlorine:

$$MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2H_2O$$

When chemical *reduction* is employed coal or carbon(II) oxide are mainly used as the reducing agents. This reaction is used to make iron (in blast furnaces), and to obtain hydrogen, and many nonferrous metals like copper, lead, and zinc:

$$Fe_3O_4\ (c) + 4CO\ (g) = 3Fe\ (c) + 4CO_2\ (g)$$
$$H_2O\ (g) + C\ (c) = CO\ (g) + H_2\ (g)$$

Hydrogen is also used as a reducing agent; the simple substance thus recovered is especially pure. It is used, for example, to reduce tungsten from WO_3, high quality iron from its oxides, and certain noble metals [Re from NH_4ReO_4 and Os from $(NH_4)_2OsCl_6$].

Metallothermic methods are commonly used. Active metals like aluminium, magnesium, sodium, calcium, etc., are employed as the reducing agents. Some examples of the reactions are given below:

aluminothermic: $Cr_2O_3 + 2Al = 2Cr + Al_2O_3$

magnesiothermic: $TiCl_4 + Mg = Ti + 2MgCl_2$

sodiothermic: $K_2BeF_4 + 2Na = Be + 2NaF + 2KF$

The method was first suggested by N. N. Beketov (1865).

Metals are usually obtained by reducing their oxides, which are obtained by appropriate treatment of the natural ores. When the ores are sulphide minerals they are roasted to oxidise them, e.g.:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

A comparatively new method in the base metal industry is to chlorinate ores with recovery of the wanted elements in the form of chlorides, which are then reduced. Titanium and other metals are prepared by this method.

Methods by which simple substances are obtained at high temperatures are known as *pyrometallurgy*.

Oxidation-reduction occurs during the thermal decomposition of compounds:

$$2KClO_3 = 2KCl + 3O_2$$
$$ZrI_4 = Zr + 2I_2$$

The obtaining and subsequent thermal decomposition of compounds is used to refine simple substances. A common method of refining metals (mainly *d* elements) to very high purity is that of iodide

process or *iodide refining* (see Fig. 222), which consists in oxidising the metal by iodine at relatively low temperatures with subsequent thermal decomposition of the iodides formed.

To prepare substances of very high purity *zone refining* is employed. The substance, e.g. a metal bar, is heated in a vessel from one end, until it melts. Impurities are more soluble in a melt than in a solid, and are therefore concentrated in the molten metal. As the source of heat is moved slowly along the vessel, the zone of the molten metal containing impurities also shifts. The impurities are thus concentrated at the other end of the bar. The metal emerging from the heated zone is crystallised. The end of the bar containing the impurities is cut off. The melting processes can be repeated to ensure very high purity.

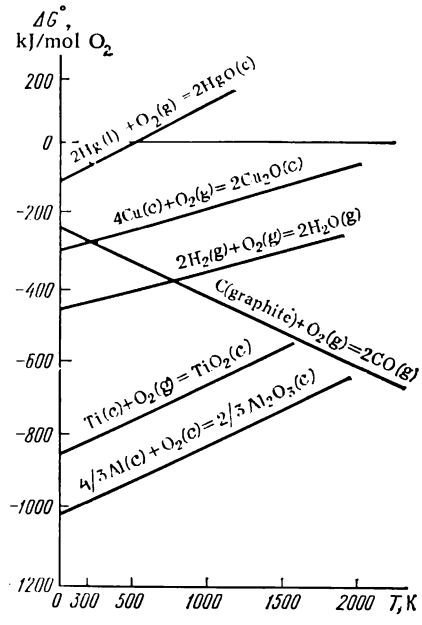


Fig. 129. Dependence of the Gibbs' energy of formation of selected oxides on temperature (in order of reducers)

Selection of reducing agents. The reducing agent for obtaining a simple substance is decided by comparing the free formation energies of the appropriate compounds. Curves of the dependence of ΔG_f of selected oxides on temperature in accordance with the equation $\Delta G = \Delta H - T\,\Delta S$ are given in Fig. 129.*

The ΔG lines for solid oxides rise with increasing temperature since the combination of gaseous oxygen with simple substances is accompanied with a decrease in volume and hence with a drop in entropy:

$$\frac{2x}{y}\,\mathrm{M\,(s)} + \mathrm{O_2\,(g)} \rightarrow \frac{2}{y}\,\mathrm{M_xO_y\,(s)}$$

The change in ΔG for water is similar:

$$2\mathrm{H_2\ (g)} + \mathrm{O_2\ (g)} = 2\mathrm{H_2O\ (l)}$$

since the volume of this system also diminishes. The Gibbs' free energy of formation of gaseous CO, on the contrary, decreases with

* The dependence of ΔG on temperature is shown in simplified form because the phase conversions (i.e. melting and boiling) of the simple substances and oxides are not taken into account.

increasing temperature because the oxidation of graphite to CO is accompanied with increasing entropy (the volume of the system increases):

$$C\ (graphite) + O_2\ (g) = 2CO\ (g), \quad \Delta S^{\circ}_{298} = 184\ J/K$$

The sequence of the lines in Fig. 129 corresponds to the increasing stability of the oxides with increasing negative values of the Gibbs' energy. A simple substance that forms a more stable oxide is therefore a potential reducer for a less stable oxide. In other words, an oxide will be reduced by that simple substance for which the ΔG line of the oxide lies below it.

Of the oxides considered, Al_2O_3 has the highest negative value of ΔG. Aluminium can consequently act as a reducer for any of these oxides. Hydrogen's reducing capacity is more limited; it can only reduce Cu_2O and HgO.

The reducing power of carbon increases significantly with rising temperature (the ΔG curve goes down). It is therefore a potential reducer for almost all oxides at high temperatures. Its reducing power with respect to TiO_2 and H_2O can be realised at temperatures of 1600 K and 750 K respectively, i.e. when ΔG becomes more negative for CO (because of the increased entropy factor) than for TiO_2 and H_2O.

As will be seen from Fig. 129, the Gibbs' free energy of the formation of HgO is negative at low temperatures and positive at high ones. This oxide can therefore only be formed at low temperatures and is decomposed into the simple substances when heated. This explains why mercury oxide is not formed when sulphide ores are roasted but the metal is liberated in the free state; for example,

$$HgS + O_2 = Hg + SO_2$$

Values of ΔG_T for oxidising simple substances with sulphur, chlorine, etc., can be compared in the same way and the necessary conditions found for obtaining simple substances by reducing the corresponding chlorides, sulphides, etc. Reactions for obtaining vanadium by reducing its oxide and dichloride with hydrogen are given below:

$$VO\ (c) + H_2\ (g) = V\ (c) + H_2O\ (g), \quad \Delta H^{\circ}_{298} = 190\ kJ$$
$$VCl_2\ (c) + H_2\ (g) = V\ (c) + 2HCl\ (g), \quad \Delta H^{\circ}_{298} = 270\ kJ$$

Both processes are endothermic. The entropy factor is more advantageous for the second reaction at elevated temperatures (two moles of gas being formed). It is therefore much easier to reduce the halide than to reduce VO by hydrogen.

The final argument in the choice of method and conditions for preparing simple substances by reduction of their compounds is the effect of temperature on the velocity of the reaction.

For industrial purposes the economic factors are decisive.

In spite of the fact that carbon (coke) can be a potential reducer of oxides of almost all metals, for instance, there are several obstacles that prevent its wider use. These are the high cost of the high process temperatures, the thermal instability of the furnace lining, the difficulty of suppressing side reactions, etc. When the purity requirements are very high, the refining of a substance often proves very expensive.

Electrochemical methods of preparing simple substances. Processes of electrochemical oxidation and reduction take place at the electrodes during the electrolysis of melts or solutions of compounds. Fluorine, chlorine, and oxygen are obtained by electrochemical (anode) oxidation, while alkali and alkaline earth metals, aluminium, and certain other metals are obtained by cathode reduction of melts of the appropriate compounds.

Hydrogen and the simple substances of most *d* elements (like Zn, Cu, Ni and Co) can be prepared by electrolysis of solutions of appropriate compounds. Electrochemical reduction is also used to refine 'crude' metals (Cr, Ni, Zn, Ag, Sn) obtained by other methods, the 'crude' metal being used as the anode and a corresponding compound of it as the electrolyte.

The electrolysis regime is chosen by the values of the electrode potential of the corresponding reaction proceeding at the electrodes.

Separation of simple substances from one another and from gangue. Simple substances that occur in nature can be separated by physical, mechanical, and chemical methods.

The *physical* methods of separation are based on differences in the substances' physical properties, e.g. on differences in boiling, melting, and freezing points, or differences in solubility, adsorbability, etc. The physical methods of separation are therefore fractionation, freezing out, absorption, adsorption, etc.

Fractional distillation is used, for example, to separate nitrogen and oxygen from liquid air. The method is based on the different boiling points of liquid nitrogen and liquid oxygen. Nitrogen, having the lower boiling point, boils out from liquid air first, thus producing a liquid air enriched with oxygen. Pure nitrogen and oxygen can be prepared by repeated liquefaction and evaporation of liquid air. A similar technique is used to separate inert gases from gaseous mixtures.

Freezing out is used to separate hydrogen and helium from natural gas mixtures. When cooled, these mixtures liquefy or solidify at different temperatures. Hydrogen and helium, having lower boiling points, remain in the gaseous state.

The *mechanical* methods include the washing of placer, for instance, to separate gold or diamond from rock. These methods are based on the different densities of the substance desired and the rock.

CHAPTER 3

Binary Compounds

3.1. Characteristics of Binary Compounds by Type of Bond

Binary compounds can be ionic, covalent, metallic, or ionic-covalent depending on the type of chemical bond.

In accordance with the regular development of atoms' electronic structure, the character of the chemical bonds (and consequently of the structure and the properties) of similar compounds change regularly within periods and groups of the periodic system. Taking binary compounds of elements of the second period as examples

	Li	Be	B	C	N	O	F
Fluorides	LiF	BeF_2	BF_3	CF_4	NF_3	OF_2	(F_2)
Oxides	Li_2O	BeO	B_2O_3	CO_2	N_2O_5	(O_2)	—
Nitrides	Li_3N	Be_3N_2	BN	C_3N_4	(N_2)	—	—

it can be shown that the polarity of the chemical bond in any of these compounds gradually diminishes from the first group to the seventh. The type of bond in the fluoride series changes from ionic in LiF, through successive decreases in polarity in BeF_2, BF_3, CF_4, NF_3, and OF_2, to nonpolar covalent bond in F_2.

The change in type of bond in the oxide series can be judged from the effective charge of oxygen in the following compounds*:

	Li_2O	BeO	B_2O_3	CO_2	N_2O_5
Effective charge on the oxygen atom δ	—0.80	—0.35	—0.24	—0.11	—0.05
Chemical nature of the oxide	Strongly basic	Amphoteric	Weakly acidic	Mediumly acidic	Strongly acidic

The degree of the ionic character of bonds in similar compounds usually increases in the main subgroups with increasing atomic number of the element, e.g.:

	Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
Effective charge on the oxygen atom δ	—0.80	—0.81	—0.89	—0.92	—0.96

A more or less marked periodicity is displayed in the properties of binary compounds in accordance with the changing type of chemical bond and structure. This will be seen, for example, in the character

* See footnote to p. 88. The effective charges given are of interest from the angle of the character of their change.

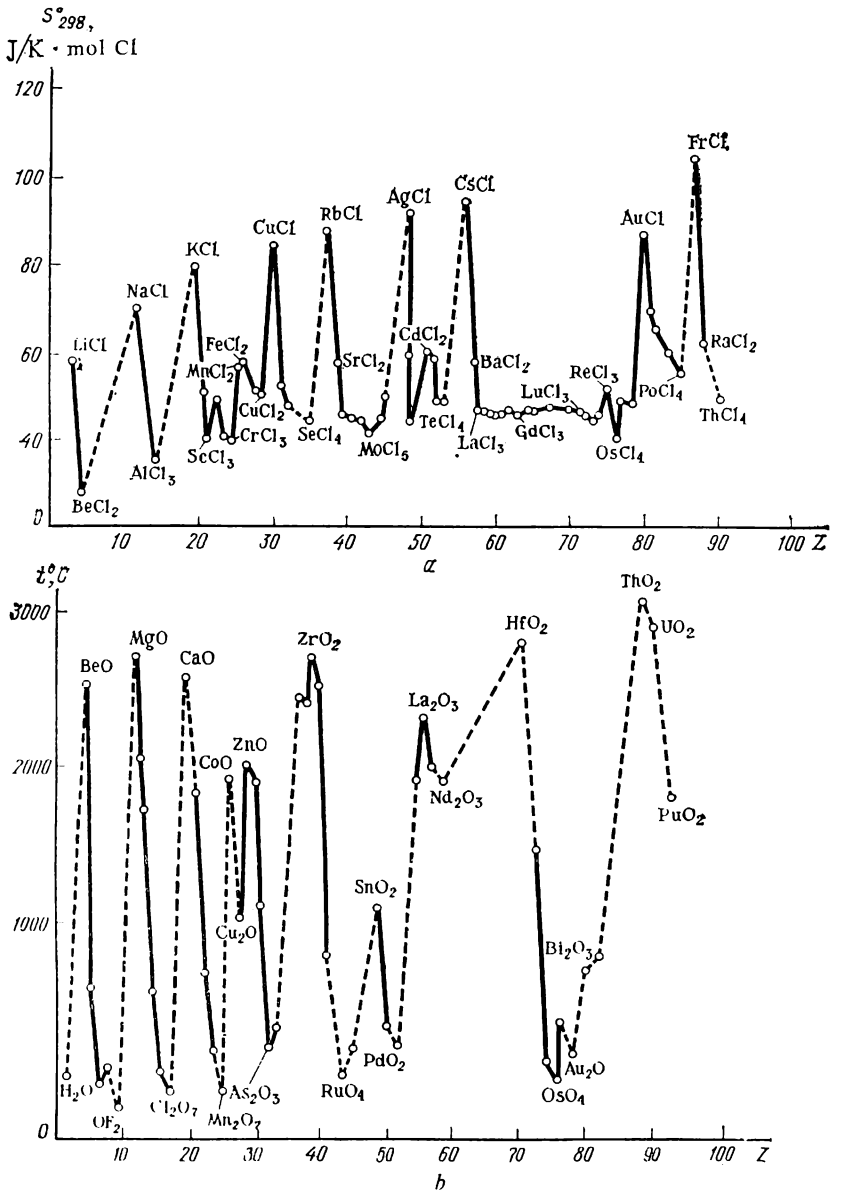
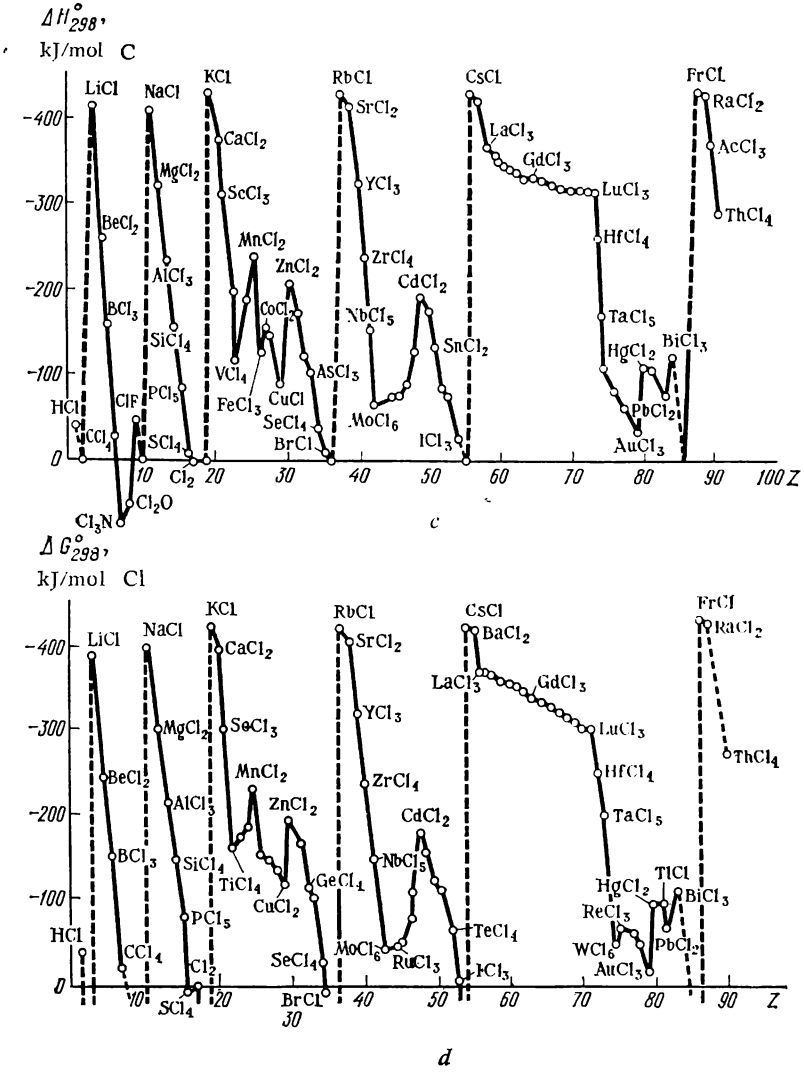


Fig. 130. Dependence of the properties of binary compounds on the atomic num-
a—standard entropy of crystalline chlorides; *b*—melting points of oxides; *c*—enthalpies of



ber of an element in a positive oxidation state:
formation of chlorides; *d*—Gibbs' energy of formation of chlorides

of changes in standard entropy, melting points, enthalpies, and Gibbs' energies of formation by periods and groups depending on

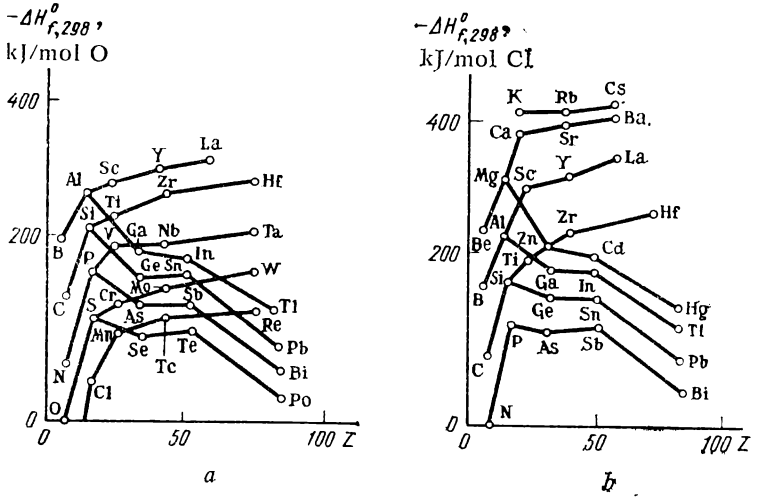


Fig. 131. Dependence of the enthalpy of formation (ΔH°_{298}) of (*a*) higher oxides and (*b*) chlorides on the atomic number of elements in a positive oxidation state

the atomic number of the element with a positive oxidation state (Fig. 130). A secondary periodicity is also displayed in the changes in parameters (Fig. 131).

3.2. Comparison of the Stability of Binary Compounds

The Gibbs' energy of the formation of compounds can be used to compare their stability.

The variation of ΔG of chlorides (ECl_n) with the atomic number of the element is shown in Fig. 130*d*. The Gibbs' energy, as will be seen, becomes less negative in each period with increasing atomic number of the element E. The stability of the chlorides therefore also decreases in that direction.

The character of changes in ΔG (calculated for one mole of atoms of the electronegative element) is about the same in the other halides, oxides, sulphides, and nitrides.

The shape of the curves is different, of course, for the various types of binary compounds. Maximum stability, for example, is observed in the halides and sulphides of group I *s* elements, and oxides of group II *s* elements. In the *s* elements, furthermore, the fluorides

are the most stable on the whole, while the chlorides are more stable than the bromides; the bromides, in turn, are more stable than the nitrides. The same difference in stability is characteristic of most *p* elements, but it is less marked. The patterns are more complicated in *d* elements.

3.3. The Acid-base Properties of Binary Compounds

The chemical properties of compounds, and their acid-base activity, also change with the chemical nature of the element. In the oxide series $Li_2O—BeO—B_2O_3—CO_2—N_2O_5$, for example, basic properties weaken and acidic properties increase with diminishing polarity of the bonds (decreasing effective negative charge on the oxygen atom δ): Li_2O is strongly basic, BeO is amphoteric, while B_2O_3, CO_2, and N_2O_5 are acidic.

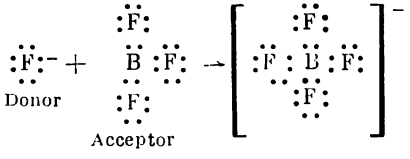
During the interaction of basic and acidic oxides, complex formation reactions are known to take place:

$$\underset{\text{Basic}}{Li_2O} + \underset{\text{Acidic}}{CO_2} = Li_2[CO_3]$$

Other compounds of the same type, with greatly differing bond polarity interact in a similar way:

$$LiF + BF_3 = Li[BF_4]$$
$$\underset{\text{Basic}}{Li_2S} + \underset{\text{Acidic}}{CS_2} = Li_2[CS_3]$$

In these reactions the lithium compounds act as donors of electron pairs (basic compounds), while the boron and carbon compounds as acceptors of these pairs (i.e. as acidic compounds), for example



The chemical properties of binary compounds depend on the chemical nature of the electropositive element: compounds of alkali and alkaline earth metals display basic properties and compounds of nonmetals acidic properties:

Li	Be	B	C	N	O	F
LiF	BeF_2	BF_3	CF_4	NF_3	OF_2	—
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	—	—
Li_3N	Be_3N_2	BN	C_3N_4	—	—	—
Basic	Amphoteric	Acidic				

In order to compare the acid-base properties of binary compounds, we can employ the ΔG of the corresponding reactions. Below are reactions of the interaction of the oxides of 3rd period elements and sodium oxide:

$$Na_2O\ (c) + Al_2O_3\ (c) = 2NaAlO_2\ (c), \qquad \Delta G^\circ_{298} = -175\ kJ$$
$$Na_2O\ (c) + SiO_2\ (c) = Na_2SiO_3\ (c), \qquad \Delta G^\circ_{298} = -197\ kJ$$
$$Na_2O\ (c) + 1/3\ P_2O_5\ (c) = 2/3\ Na_3PO_4\ (c), \qquad \Delta G^\circ_{298} = -371\ kJ$$
$$Na_2O\ (c) + SO_3\ (c) = Na_2SO_4\ (c), \qquad \Delta G^\circ_{298} = -522\ kJ$$
$$Na_2O\ (c) + Cl_2O_7\ (g) = 2NaClO_4\ (c) \qquad \Delta G^\circ_{298} = -587\ kJ$$

As will be seen from the values of ΔG, the acidic properties of the oxides rise steeply in the series Al—Si—P—S—Cl along with their increasing nonmetallic character.

In the same way it can be shown that acidic properties increase in the same series of elements in other binary compounds, e.g.

$$NaF\ (c) + MgF_2\ (c) = NaMgF_3\ (c), \qquad \Delta G^\circ_{298} = -14\ kJ$$
$$NaF\ (c) + 1/3\ AlF_3\ (c) = 1/3\ Na_3AlF_6\ (c), \qquad \Delta G^\circ_{298} = -26\ kJ$$
$$NaF\ (c) + 1/2\ SiF_4\ (c) = 1/2\ Na_2SiF_6\ (c), \qquad \Delta G^\circ_{298} = -51\ kJ$$

Compounds of elements of the same type display a community of properties in other reactions as well, for example, in solvolysis (hydrolysis), ammonolysis, etc. Binary compounds of the alkali and alkaline earth metals, for instance, are barely hydrolysed, or produce an alkaline medium when they are:

$$NaCl + HOH \rightleftarrows \text{practically no hydrolysis}$$
$$Na_2O + HOH \rightleftarrows 2NaOH$$
$$Na_2S + HOH \rightleftarrows NaOH + NaSH$$

The hydrolysis of binary compounds of nonmetals, on the contrary, is irreversible and results in acids:

$$BCl_3 + 3HOH = H_3BO_3 + 3HCl$$
$$B_2O_3 + 3HOH = 2H_3BO_3$$
$$B_2S_3 + 6HOH = 2H_3BO_3 + 3H_2S$$

Compounds in which two elements act as oxidants, i.e. oxyhalogens, nitrohalogens, oxysulphides, etc., can be classified in a similar way. Carbon(IV) oxysulphide, COS, for example, is an acidic compound, as is shown by its reaction with water (on heating) and with basic compounds:

$$COS + 2H_2O = H_2CO_3 + H_2S$$
$$CaO + COS = Ca[CO_2S]$$

Not only individual atoms play the role of negatively polarised constituents (oxidants) but also groups (for example, OH^-, SH^-, NH_2^-, CN^-) capable of in-

dependent existence as ions:

Hydroxides	Hydrosulphides
NaOH sodium hydroxide	NaSH sodium hydrosulphide
$Zn(OH)_2$ zinc hydroxide	$Zn(SH)_2$ zinc hydrosulphide
$B(OH)_3$ boron hydroxide	$B(SH)_3$ boron hydrosulphide
Dihydronitrides	**Cyanides**
$NaNH_2$ sodium dihydronitride	NaCN sodium cyanide
$Zn(NH_2)_2$ zinc dihydronitride	$Zn(CN)_2$ zinc cyanide
$B(NH_2)_3$ boron dihydronitride	$B(CN)_3$ boron cyanide

The chemical bond between the radical and the positively polarised atom (and hence the properties of the compounds concerned) changes regularly in the groups and periods of the periodic system according to the nature of the electropositive element, e.g.

Rb	Sr	In	Sn	Sb	Te
RbOH	$Sr(OH)_2$	$In(OH)_3$	$Sn(OH)_4$	$Sb(OH)_5$	$Te(OH)_6$
Basic hydroxides		Amphoteric hydroxides		Acidic hydroxides	

In this series a transition from ionic hydroxides of the alkali and alkaline earth metals to covalent hydroxides of nonmetallic elements can be observed; the chemical nature of the hydroxides changes accordingly, as can be seen from the following reaction:

$$\underset{\text{Basic}}{2RbOH} + \underset{\text{Acidic}}{Sn(OH)_4} = Rb_2[Sn(OH)_6]$$

3.4. Intermetallic Compounds

The problems of the chemical interaction of metals and metals, and metals and nonmetals (provided the reaction products retain metallic properties) is studied by the branch of inorganic chemistry known as *metallochemistry*.

If we arrange metals in order of their increasing chemical interaction, the following series will be obtained:

(a) metals that do not react with one another (either in the liquid or solid states);

(b) metals that dissolve one another in the liquid state and form a eutectic in the solid state;

(c) metals that form liquid and solid solutions of any composition with one another;

(d) metals that form one or more *intermetallic* compounds with one another.

Solid metal solutions. Metals have a marked tendency to dissolve metals, and to a lesser degree nonmetals. This tendency is the result of their extremely nonlocalised bonds. Because of its electron deficit (see Fig. 75), the valence band of a metallic crystal can accept a certain number of additional electrons without alteration of the crystal's structure and metallic properties. In a crystal of silver, the atoms of which have one s^1 valence electron, for example, the

electron concentration (the ratio of the total number of valence electrons to the total number of atom in the crystal) is unity, but may rise to 1.4 because of electrons belonging to atoms of other elements.

This rise in electron concentration (by 40 per cent) in the valence band corresponds to a metal's maximum solubility in silver; a solid solution with silver, for example, can contain (mole per cent) up to 40 per cent of Cd (s^2), 20 per cent of In (s^2p^1), 13.3 per cent of Sn (s^2p^2), or 10 per cent of Sb (s^2p^3).

It will be seen that the solubility of metals in silver diminishes with an increasing number of valence electrons. But when gold (one s^1 valence electron) is dissolved in silver, the electron concentration is not altered; for that reason gold and silver can dissolve one another in any proportion.

The addition of electrons above the permissible optimum leads to energy instability of the given type of metal-solvent crystal structure, and the formation of a structure of another type, which indicates that the solid solution has been converted into an intermetallic compound, or (when the valence band is completely filled) into a compound with a covalent or ionic bond.

The formation of energy zones is only possible provided the overlapping orbitals correspond in energy and spatial arrangement (see Fig. 75). The solubility of substances in metals therefore depends not only on the number of valence electrons but also on their type (*s*, *p*, *d* or *f*) and energy state. Because of the complicated interconnections of these factors in polyatomic systems, the method of calculating maximum solubility described above is not possible in most cases.

As we have already mentioned, the formation of solid solutions is favored by closeness of the initial substances' chemical properties, atomic radii, and type of crystal lattice (see p. 141). If one of these conditions is not observed, solid solutions will only be formed by the components within certain limits of concentration or not at all. The maximum solubility of certain metals in nickel (d^8s^2, r = = 0.124 nm), for example, can be expressed in the form of the following series:

	Co	Fe	Mn	Cr	V	Ti	Sc	Ca	K
Valence electrons	d^7s^2	d^6s^2	d^5s^2	d^5s^1	d^3s^2	d^2s^2	d^1s^2	s^2	s^1
Atom radius of metals, nm	0.125	0.126	0.130	0.127	0.134	0.146	0.164	0.197	0.236
Solubility, mole/per cent	100	100	100	50	43	15	?	Practically insoluble	

Nickel, cobalt, iron, and manganese, which are closely related in chemical properties and atomic size, form a continuous series of solid solutions with each other. In the Cr—V—Ti series, the solubility of the metal in nickel decreases with increasing difference in chemical

properties. Calcium and potassium, which differ greatly from nickel in properties and atomic dimensions, generally do not form solid solutions with it.

Intermetallic compounds. In contrast to solid solutions, intermetallic compounds, as a rule, have complicated crystal structures differing from those of the parent metals. Their properties also differ substantially from those of the initial components; in ordinary conditions, for example, intermetallic compounds are inferior to pure metals as regards electrical and thermal conductivity, but are superior to the parent metals as regards hardness and melting points, as the following table illustrates:

	Mg	β-Sn	Mg_2Sn
M. p., °C	650	232	778
Electrical conductivity *	21	8	0.1
Width of forbidden zone, eV	Absent		0.34

All this shows that intermetallic compounds can be considered compounds with mixed interatomic bonds (metallic, covalent, and ionic). The relative proportions of one type of bond or another varies within wide limits in the different intermetallic compounds.

The diversity of type of bond and crystal structure accounts for intermetallic compounds' broad spectrum of physicochemical, electrical, magnetic, mechanical, and other properties. Their electrical properties, for example, may sometimes vary from superconductivity in liquid helium to semiconductivity in ordinary conditions.

The mechanical properties of intermetallic compounds are quite unique and are very sensitive to the effect of temperature. In ordinary conditions, most of them are very hard and brittle, but at temperatures 70 to 90 per cent of their melting point they behave like plastic bodies, principally because the proportion of metallic bonds increases with heating.

Many intermetallic compounds have the high heats of formation and chemical stability.

Intermetallic compounds are insoluble in water but several (like certain metals) are soluble in nonaqueous solvents, liquid ammonia in particular. They then behave like electrolytes, i.e. yield ions on dissolving and enter into double exchange reactions

$$2Ca(NO_3)_2 + K_4Pb = Ca_2Pb + 4KNO_3$$

$$4Zn(CN)_2 + 10Na = 2NaZn_4 + 8NaCN$$

During electrolysis of solutions or melts of intermetallic compounds, relatively more electronegative metal is deposited at the anode and more electropositive at the cathode. During electrolysis of a solution of Na_4Pb_9 in ammonia, for example, sodium is deposited at the cathode and lead at the anode. During

* Here and throughout the text the electrical conductivity of mercury is taken as unity.

the electrolysis of molten KNa_2, potassium is deposited at the cathode and sodium at the anode. During the interaction of metals dissolved in nonaqueous solvents (e.g. liquid ammonia), on the contrary, intermetallic compounds are produced:

$$4Na + 9Pb = Na_4Pb_9 \text{ (green solution)}$$

$$3Na + 7Sb = Na_3Sb_7 \text{ (red solution)}$$

$$3Na + 7Bi = Na_3Bi_7 \text{ (brown solution)}$$

Composition and structure of intermetallic compounds. When metallic bonds predominate, the structure and composition of intermetallic compounds can be determined from their electron concentrations. It has been found, for instance, that the electron concentration of some is 1.5 with a body-centred cubic structure and 1.75 with a hexagonal structure.

As an example, let us consider what combinations of zinc and copper atoms give rise to intermetallic compounds with body-centred cubic or hexagonal structures. Since copper (s^1) has one valence electron and zinc (s^2) two, an electron concentration of 1.5 is possible only for a compound with an average CuZn composition (i.e. when there are three valence electrons for every two atoms). An electron concentration of 1.75 arises when the composition of the compound is $CuZn_3$ (seven valence electrons for every four atoms).

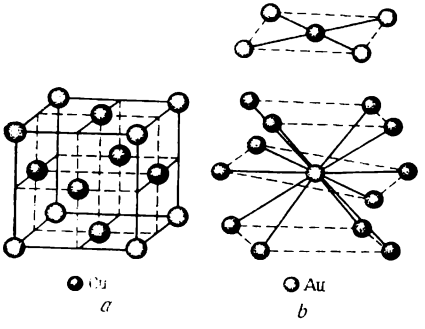


Fig. 132. Crystal lattice of (*a*) Cu_3Au and (*b*) the mutual coordination of atom in a crystal

It can be demonstrated in the same way that compounds with an AgZn, AgMg, Cu_3Al, or Cu_5Sn composition have a body-centred crystal lattice, while Ag_5Al_3, $Ag_{13}Sb_3$, Cd_3Li, Cu_3Si have a hexagonal structure.

The pattern for most intermetallic compounds, however, particularly of *d* elements, would seem to be more complicated, and it is still impossible to predict their composition and structure theoretically.

Information on the composition and structure of intermetallic compounds is usually obtained experimentally. The crystal lattice of Cu_3Au is shown in Fig. 132*a*. The gold atoms are located at the apexes of the cube while the copper atoms are at the centres of the faces. Consequently, each gold atom is coordinated with 12 copper atoms, and each copper atom with four golds (Fig. 132*b*), which corresponds to an average formula Cu_3Au.

CHAPTER 4

Ternary Compounds

4.1. Derivatives of Anion Complexes

As we have seen, the interaction of binary compounds differing widely in their chemical properties yields new compounds among which those consisting of three elements are the simplest:

$$NaF + BF_3 = Na[BF_4]$$

$$\underset{\text{Basic}}{Na_2O} + \underset{\text{Acidic}}{CO_2} = Na_2[CO_3]$$

These compounds may be ionic, ionic-covalent, or covalent depending on the chemical bond between their inner and outer spheres. If an anion complex is sufficiently stable, the compounds are like binary ones as regards their acid-base properties. Derivatives of the alkali and alkaline earth metals are thus basic while derivatives of nonmetals are acidic. This is confirmed by their solvolysis and the reactions between derivatives of anion complexes of different acid-base properties, e.g.

$$\underset{\text{Basic}}{RbNO_3} + \underset{\text{Acidic}}{INO_3} = Rb[I(NO_3)_2]$$

$$\underset{\text{Basic}}{RbNO_3} + HOH = \text{practically no hydrolysis}$$

$$\underset{\text{Acidic}}{INO_3} + HOH = HIO + HNO_3$$

The stability of derivatives of anion complexes greatly depends on the nature of the atoms in their outer sphere, as they are more or less responsible for the contrapolarisation (i.e. weakening of the inner bonds) of the complexes. The greater the atoms' tendency to form covalent bonds (the higher their electronegativity), moreover, the greater as a rule is their counterpolarising power. This will easily be seen from a comparison of the temperature and ΔG°_{298} of decomposition of the corresponding compounds, for example, oxycarbonates of group II *s* elements:

$$ECO_3\ (c) = EO\ (s) + CO_2\ (g)$$

	Ba	Sr	Ca	Mg	Be
Electronegativity	0.89	0.95	1.00	1.31	1.57
Carbonate	$BaCO_3$	$SrCO_3$	$CaCO_3$	$MgCO_3$	$BeCO_3$
Decomposition temperature, °C	1300	1100	840	400	100
ΔG°_{298} of decomposition, kJ/mol	216	183	130	65	—30

$MgCO_3$ (ΔG = 65 kJ/mol), when heated, breaks down into MgO and CO_2 at 300 °C, while $BaCO_3$ (ΔG = 216 kJ/mol) only decomposes appreciably into BaO and CO_2 at 1300 °C.

The effect of the nature of outer sphere atoms on the stability of compounds can be demonstrated by the reaction of $AlCl_3$ with MCl.

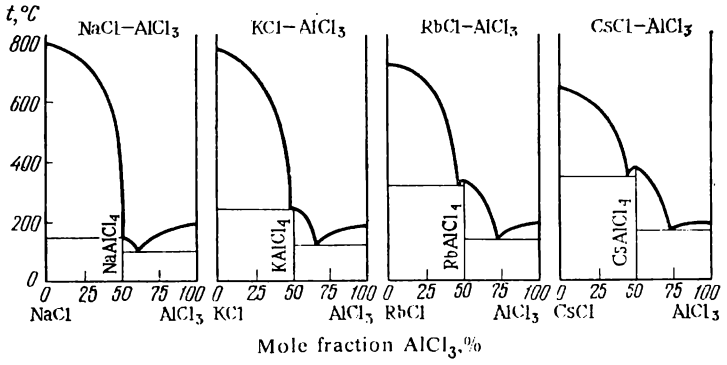
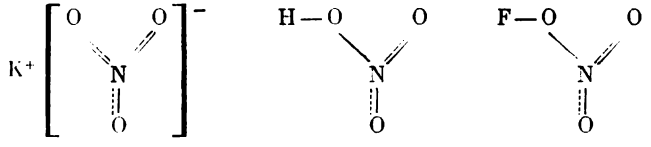


Fig. 133. Phase diagram of the MCl—$AlCl_3$ system

The phase diagrams (Fig. 133) show that the stability of the $M[AlCl_4]$ compounds increases in the series NaCl—$AlCl_3$, KCl—$AlCl_3$, RbCl—$AlCl_3$, and CsCl—$AlCl_3$, which corresponds to a decrease in contrapolarising action in the series Na^+—K^+—Rb^+—Cs^+, i.e. to a heightened tendency to form ionic bonds.

The decreasing thermal stability and increasing electronegativity of the outer sphere atom in the series KNO_3—HNO_3—FNO_3 can be explained likewise:



The K^+ and NO_3^- ions are isolated from each other in KNO_3. In covalent HNO_3 and FNO_3 electron density (π bonding) is redistributed through the formation of the H—O and F—O bonds in the NO_3^- ion, which lowers the stability of the ion. Covalent HNO_3 thus begins to decompose at ordinary temperatures and illumination while the ionic compound KNO_3 breaks down only at temperatures above 400 °C; FNO_3 can only exist at temperatures below —5 °C.

Because of the outer sphere's contrapolarising action cation derivatives of nonmetals and complex anions are quite unstable and are only known for relatively weakly electronegative elements with low oxidation states, e.g. I (I), I (III), Te (II), Sb (III).

The well-known fact of the lower stability of acids with complex acidic radicals compared with their salts can be explained in the same way. It will be remembered, for example, that the salts Na_2CO_3, K_2SO_3, $KClO_3$, and KBF_4 are quite stable, while analogous compounds of hydrogen, like H_2CO_3, H_2SO_3, $HClO_3$, and HBF_4 have not been obtained in the free state because of their instability.

4.2. Mixed Compounds, Solid Solutions, Eutectics

Several types of interaction between compounds are possible, depending on the nature of the initial substances. During the interaction of compounds that differ greatly in their chemical properties a new compound is formed (examples of this interaction were discussed above) (see p. 256).

To the extent that the difference in the chemical properties of the interacting compounds is less marked, the conditions for the forming of complex anions deteriorate and *mixed compounds*, or *solid solutions* or *eutectics* are formed.

Mixed compounds are obtained through the interaction of compounds of elements equally susceptible to complex formation, for example:

$$CuS + FeS = CuFeS_2 \text{ (chalcopyrite)}$$

$$MgO + Al_2O_3 = \underset{\text{Mixed compound}}{MgAl_2O_4} \text{ (spinel)}$$

Mixed compounds are polymers in which the atoms of both the electropositive elements act as complexing agents, i.e. are chemically equivalent. The crystal of KBF_4, for example, has an insular structure and the K^+ and BF_4^- ions can be distinguished in it, while the mixed compound $CuFeS_2$ (*chalcopyrite*) is a coordinated polymer, and the Cu and Fe atoms in its crystal lattice are in a state of sp^3 hybridisation and are included in the tetrahedra of the sulphur atoms as CuS_4 and FeS_4 unit cells (complexes) (Fig. 134), i.e. chalcopyrite, $CuFeS_2$, is a mixed sulphide of copper(II) and iron(II).

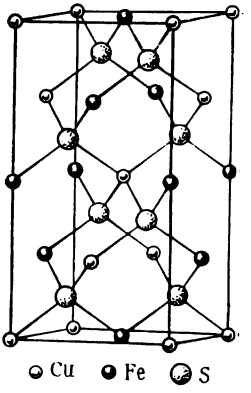


Fig. 134. Crystal lattice of chalcopyrite $CuFeS_2$

Spinel, $MgAl_2O_4$, is a mixed oxide of magnesium(II) and aluminium(III). It, too, is a coordinated polymer and its crystals are formed by tetrahedral MgO_4 and octahedral AlO_6 unit cells. Compounds of the composition $\overset{+2}{M}(\overset{+3}{M}O_2)_2$, in which $\overset{+2}{M}$ is Mg, Mn, Fe, Co, Ni, and $\overset{+3}{M}$ is Al or Cr, have the same structure.

In addition to a structure of the chalcopyrite and spinel types, *ilmenite*, *perovskite*, and other structural types (see p. 117), are very characteristic of mixed compounds (mixed oxides, sulphides, halides, nitrides, etc.).

When the electropositive elements of the interacting compounds can form unit cells (complexes) similar in structure and stability, solid substitutional solutions are obtained:

$$KNO_3 + RbNO_3 = \underset{\text{Solid solution}}{KNO_3 - RbNO_3}, \qquad MnCl_2 + FeCl_2 = \underset{\text{Solid solution}}{MnCl_2 - FeCl_2}$$

Compounds of elements similar in chemical properties but differing in the size and structure of their atoms (ions) do not interact chemically but produce a mechanical mixture of crystals or eutectic. A eutectic mixture is formed, for example, through the simultaneous crystallisation of KCl ($r_{K^+} = 0.133$ nm) and LiCl ($r_{Li^+} = 0.068$ nm):

$$LiCl + KCl = \underset{\text{Eutectic}}{LiCl + KCl}$$

The effect of the nature of the interacting compounds on the character of the products formed can be illustrated by phase diagrams of the corresponding systems (Fig. 135). A solid solution is formed,

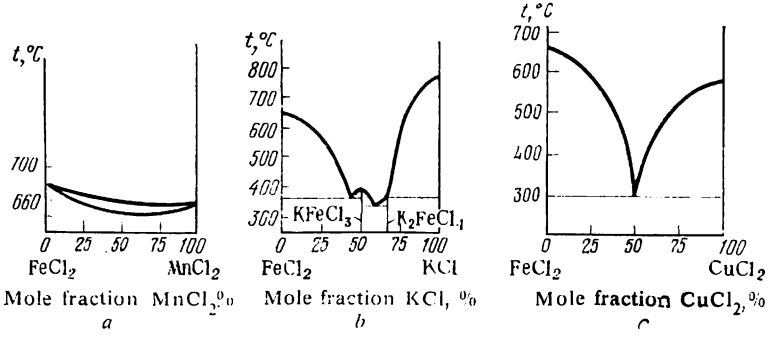


Fig. 135. Phase diagram of a system:
a—solid solution; *b*—with a chemical compound; *c*—with a eutectic

for instance, in a system of chemically and structurally similar compounds of neighbouring elements in the periodic system ($MnCl_2$—$FeCl_2$), while a eutectic is formed in a system of compounds that are chemically similar but different as regards structure $FeCl_2$—$CuCl_2$ ($FeCl_2$ has a layer structure and $CuCl_2$ a chain structure). Finally, a new chemical compound is formed in a system consisting of compounds differing markedly in their chemical nature (KCl—$FeCl_2$).

CHAPTER 5

Nonstoichiometric Compounds

5.1. Compounds of Variable Composition

In addition to compounds that obey the laws of constant composition and multiple proportions, there are many of *variable composition*—solid oxides, sulphides, nitrides, carbides, etc.

The theory of compounds of variable composition originated from concepts of the structure of a real crystal. It is commonly taken that in an ideal crystal *all* points of the lattice are occupied by the atoms (ions), and that *there are no atoms* (ions) *outside* this system of points. But the experimentally observed properties of solids, of course, do not always agree with this notion. In the real crystals of, for example, a binary compound AB, there can be vacant lattice points corresponding to the A or B atom (ion); furthermore, surplus A or B atoms (ions) can be located in the interstices between lattice points. The crystal lattice of titanium carbide TiC, for example, is preserved even when 40 per cent of the carbon atoms are missing. Its composition may therefore vary from $TiC_{0.6}$ to TiC and depends on the conditions of the synthesis.

Lead(II) sulphide, the formula of which is usually written PbS, in fact has a composition between $Pb_{0.9995}S$ and $PbS_{0.9995}$. The composition of titanium(II) oxide TiO varies between $Ti_{0.7}O$ and $TiO_{1.3}$, while that of titanium(IV) oxide TiO_2 is between $TiO_{1.9}$ and $TiO_{2.0}$, and so on.

Thus, in contrast to compounds of constant composition characterised by whole-number stoichiometric coefficients, the stoichiometric coefficients of compounds of variable composition are fractional.

Compositions within the range of limiting values of defects in stoichiometric composition are known as a compound's region of *homogeneity*. The region of homogeneity of titanium(II) oxide, for instance, is very wide while that of lead(II) sulphide is quite narrow.

The forming of defects in a crystal lattice is, of course, an endothermic process but, like any disorder, is accompanied with increasing entropy. Therefore, in accordance with $\Delta G = \Delta H - T\Delta S$, there must be defective positions or vacancies in a real crystal at any temperature other than absolute zero. Within the region of homogeneity, the properties of compounds of variable composition (enthalpy and Gibbs' function, entropy, electrical conductivity, etc.) change continually. For example, the enthalpy and Gibbs' free energy for zirconium nitride are as follows (kJ/mol):

	$ZrN_{0.56}$	$ZrN_{0.69}$	$ZrN_{0.74}$	$ZrN_{0.89}$	$ZrN_{1.0}$
$\Delta H^\circ_{f,\,298}$	−235	−287	−302	−344	−365
$\Delta G^\circ_{f,\,298}$	−220	−268	−281	−319	−336

N.S. Kurnakov suggested calling the compounds of variable composition *berthollide compounds* and those with a constant composition *daltonide compounds.** Any solid compound, as a matter of fact, except those with molecular lattices (H_2O, CO_2, CCl_4, H_3N) are compounds of variable composition. Even NaCl, depending on the conditions, can have deviations from its stoichiometric composition. When sodium chloride is heated, for instance, its sodium atoms are incorporated inside the lattice of NaCl, which gives the crystal a bright blue colour. Whether a substance is classed as a compound of constant or variable composition depends on the sensitivity of the research techniques. The deviations from stoichiometric composition are often so insignificant that they cannot be detected by chemical analysis. Study of substances' properties, like electrical conductivity, colour, magnetic and other properties, however, indicates whether a compound is of variable composition. Variable composition is most common among the compounds of *d* elements.

5.2. Inclusion Compounds

Certain crystalline hydrates with a large number of water molecules, e.g. $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, are a special case of an ordered inclusion (interstitial solution) of the salt/ice type, known as *tectohydrates*. They have the structure of ice stabilised by the binding effect of electrostatically interacting ions of opposite sign, as a result of which their melting point is rather higher than that of ice.

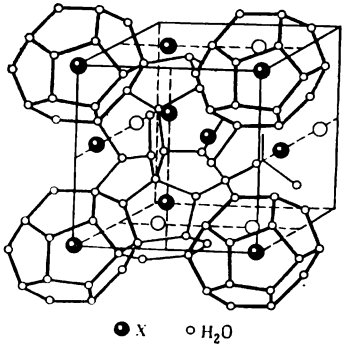


Fig. 136. Structure of an X·5.75 H_2O clathrate

Rather similar to tectohydrates are *inclusion compounds*, i.e. systems formed as a result of the reversible inclusion of one substance ('guest') in the free spaces of the crystal of another substance ('host'), the intermolecular interaction of the 'guest' molecules with the components of the crystal being of secondary importance.

Inclusion compounds are also known as *clathrates*. These include, for example, '*gas hydrates*' formed by the occlusion of Cl_2, CH_4, H_2S, Ar, Xe, SO_2 or other molecules in the interstices of an ice crystal. One variety of ice, for example, has eight holes per 46 mole-

* In honour of John Dalton, who widely applied molecular-atomic theory to chemical phenomena, and Claude Louis Berthollet, who was the first to suggest that there might be compounds that did not obey the laws of constant composition and multiple proportion.

cules of water; hence the average composition of these clathrate type crystalline hydrates is $X \cdot 5.75\ H_2O$, or (in round figures) $X \cdot 6H_2O$ (where X is a 'guest' molecule). The structure of a gas hydrate of this composition is shown in Fig. 136. Gas hydrates with an $X \cdot 7.75H_2O$ ($X \cdot 8H_2O$) composition also occur.

Gas hydrates are solid crystalline substances outwardly resembling snow or porous ice. The first gas hydrate, chlorine hydrate, $Cl_2 \cdot 6H_2O$ (Davy, 1811), was obtained by chilling an aqueous solution saturated with chlorine to 9 °C.

Inclusion compounds are being widely studied today. Gas clathrates, in particular, are of great practical and theoretical interest. They are formed during several processes in the oil-refining, gas, and petrochemical industries; hydrocarbon hydrates are a nuisance in pipelines and apparatus. To prevent clogging, it is necessary to know the conditions (temperature, pressure, and other parameters) in which hydrates with various composition of the gaseous phase are formed.

The formation of gas clathrates with their subsequent destruction is employed, for example, for separating gases (hydrocarbons, noble gases), isomeric compounds, and for desalinating sea water. Clathrates are used as a convenient form of storing gases, since one volume of a clathrate can hold up to 200 volumes of a gas.

The desalination of sea water is based on the high stability of hydrocarbon clathrates. When gas is forced into salt water (at a temperature of 1.1 °C to 24 °C and a pressure of 0.4 to 7 MPa) solid hydrocarbon clathrates are formed. Crystalline hydrates of propane are formed, for example, at 1.7 °C and 0.4 MPa. The precipitated hydrates are separated out, washed and then decomposed at a temperature of 7.2 °C and pressure of 0.5 MPa, yielding potable water. The recovered propane is recycled to form the clathrate. This method of the desalination of sea water is highly efficient.

In nature clathrates often act as natural gas reservoirs. Soviet scientists (A.A. Trofimuk *et al.*) have discovered solid methane gas hydrate deposits (an important source of a valuable raw material) at a considerable depth in permafrost regions.

II

THE CHEMISTRY OF *s* AND *p* ELEMENTS

The elements in the main subgroups of the periodic system are *s* and *p* elements. Each period begins with two *s* elements; the last six elements in the period (except the first period) are *p* elements.

CHAPTER 1

General Patterns

The valence electrons and orbitals of *s* and *p* elements are in the outer shells of the atoms. The number of valence electrons corresponds to the number of the group to which the element (except H and He) belongs:

Group	I	II	III	IV	V	VI	VII	VIII
Electronic configuration of the valence shell	s^1	s^2	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6

The character of the changes in atomic radii, ionisation energies, and electron affinities within periods and groups was shown earlier in Figs. 17, 12, and 14. As will be seen from them, the orbital radii of atoms decrease in the period with increasing atomic number while the ionisation energy on the whole increases.

At the same time, the size of atoms in general increases and the ionisation energy decreases in the subgroups of elements as their atomic numbers increase. The character of the changes in electron affinity within the periods and subgroups of *s* and *p* elements is quite the opposite (see Fig. 14). From Fig. 15 it follows that as we pass from group I to group VII the electronegativity of the elements increases in the period and decreases downward in the subgroups. Such are the general tendencies in the change of the constants we are

concerned with. As we have already said, an *inner* periodicity can be seen in the character of the changes in properties of the elements in a period and a *secondary* periodicity in a subgroup (see Fig. 18).

1.1. Oxidation States of *s* and *p* Elements

Evidence of the non-monotonous character of the changes in the properties of elements in the main subgroups is, for example, the energy differences in the outer *s* and *p* orbitals (Table 28), and the dependence of the oxidation states (Table 29) and coordination numbers (Table 30) of *s* and *p* elements on their atomic numbers.

Table 28. **The Energy Difference (eV) of the Outer *s* and *p* Orbitals in the Main Subgroups**

2nd period	Li	Be	B	C	N	O	F	Ne
	1.9	2.8	4.6	5.3	6.0	14.9	20.4	26.8
3rd period	Na	Mg	Al	Si	P	S	Cl	Ar
	2.1	2.7	4.5	5.2	5.6	9.8	11.6	13.5
4th period	K	Ca	Ga	Ge	As	Se	Br	Kr
	—	—	5.9	6.7	6.8	10.4	12.0	13.2
5th period			In	Sn	Sb	Te	I	Xe
			5.2	5.8	6.6	8.8	10.1	—
6th period			Tl	Pb	Bi	Po	At	Rn
			(7)	(9)	(10)	(12)	(16)	—

Table 29. **Oxidation States of *s* and *p* Elements**

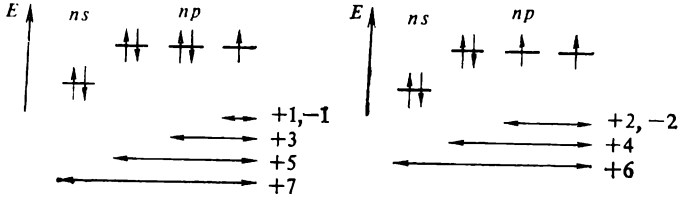
Group	I	II	III	IV	V	VI	VII	VIII
Valence electrons	s^1	s^2	s^2p^1	s^2p^2	s^2p^3	s^2p^4	s^2p^5	s^2p^6
Element	Li	Be	B	C	N	O	F	Ne
Oxidation state	1	2	3	4, 2 −4	5, 3 −3	2 −2	— −1	— —
Element	Na	Mg	Al	Si	P	S	Cl	Ar
Oxidation state	1	2	3	4, 2 −4	5, 3 −3	6, 4 −2	1, 3, 5, 7 −1	— —
Element	K	Ca	Ga	Ge	As	Se	Br	Kr
Oxidation state	1	2	3	4, 2 −4	5, 3 −3	6, 4 −2	1, 3, 5, 7 −1	2, 4 —
Element	Rb	Sr	In	Sn	Sb	Te	I	Xe
Oxidation state	1	2	3	4, 2 −4	5, 3 −3	6, 4 −2	1, 3, 5, 7 −1	2, 4, 6, 8 —
Element	Cs	Ba	Tl	Pb	Bi	Po	At	Rn
Oxidation state	1	2	1, 3	2, 4 −4	3, 5 −3	4, 6 −2	5, 7 −1	(2, 4, 6, 8) —

Table 30. **Fluorine and Oxy Complexes of Selected Elements**

Period	Group							Number of electron pairs of the central atom	Coordination number of the central atom
	II	III	IV	V	VI	VII	VIII		
2	BeF_4^{2-}	BF_4^-	CF_4^0	NF_4^+				4	4
3		AlF_6^{3-}	SiF_6^{2-}	PF_6^-	SF_6^0	ClF_6^+		6	6
4		GaF_6^{3-}	GeF_6^{2-}	AsF_6^-	SeF_6^0			6	6
2		BO_3^{3-}	CO_3^{2-}	NO_3^-				3	3
			SiO_4^{4-}	PO_4^{3-}	SO_4^{2-}	ClO_4^-		4	4
4			GeO_4^{4-}	AsO_4^{3-}	SeO_4^{2-}	BrO_4^-		4	4
5			SnO_6^{8-}	SbO_6^{7-}	TeO_6^{6-}	IO_6^{5-}	XeO_6^{4-}	6	6

In *s* and *p* elements the valence electrons are in the outer shell. When all the valence electrons are involved in the formation of bonds, the element displays its highest oxidation state, which is numerically equal to the number of the group of the periodic system to which it belongs. The 'even number' rule holds for the oxidation states of *s* and *p* elements. Those compounds are more energy-wise in which the elements of odd-numbered groups display an odd oxidation state and the elements of even groups show even oxidation states.

In other words, odd oxidation states are characteristic of elements of the odd-numbered groups of the periodic system and even oxidation states of the elements of the even-numbered groups (Table 29), for example,



The highest oxidation state of the elements in the main subgroups becomes less stable as we pass from group I to group VIII, which is due to the increasing energy differences between the *s* and *p* orbitals of the outer shell of the atom in this direction and hence to the decreasing probability of ns^2 electrons being involved in the formation of the chemical bond. Thus, a steep increase in the energy difference between 3*s* and 3*p* orbitals in the series Si (5.2 eV)—P (5.6 eV)—

S (9.8 eV)—Cl (11.6 eV) leads to an abrupt decline in stability of the oxy ions formed by them:

$$SiO_4^{4-} \quad PO_4^{3-} \quad SO_4^{2-} \quad ClO_4^-$$

The secondary periodicity is clearly seen in the character of changes in the energy difference between the *ns* and *np* orbitals in the subgroup. Table 28 shows that this difference is greater for elements of the fourth period than for those of the 3rd and 5th periods. Hence the compounds corresponding to the highest oxidation state of 3*p* and 5*p* elements should be more stable than those of 4*p* elements. What has been said above explains the experimentally found stability series of the type of

$$PCl_5 > AsCl_5 < SbCl_5,$$
$$SF_6 > SeF_6 < TeF_6,$$
$$ClO_4^- > BrO_4^- < IO_4^-$$

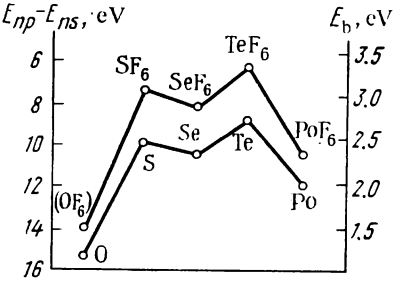


Fig. 137. Energy difference between the *ns* and *np* levels of the atoms of Group VI *p* elements and the mean bond energy in molecules of their hexafluorides

The difference is especially great between the energies of 6*s* and 6*p* orbitals, which explains the instability of the highest oxidation state of *p* elements of the 6th period. Since it is difficult to involve the $6s^2$ electrons of *p* elements of the 6th period in the formation of chemical bonds, the effect is referred to as the 'inert 6*s* pair effect'.

The change in energy differences between the *ns* and *np* orbitals of elements of this subgroup and its effect on the properties of analogous compounds are shown in Fig. 137, in which it will be seen that the mean bond energy in hexafluorides of Group VI *p* elements changes with increasing atomic number in the reverse sequence as the energy difference between *ns* and *np* orbitals.

1.2. Coordination Numbers of *s* and *p* Elements

The valence orbitals of *s* and *p* elements are the outer energy levels, i.e. one *ns* and three *np* orbitals. True, there are vacant *nd* orbitals in elements of the 3rd and subsequent periods, but calculations indicate that their energy states are so high that the probability of their being involved in the formation of chemical bonds is quite low.

Let us consider the energy diagram of an octahedral molecule of sulphur hexafluoride SF_6 (Fig. 138). The figure shows that this molecule's bonds are formed by one $3s$ and three $3p$ orbitals of the sulphur atom and six $2p$ orbitals of the six fluorine atoms. According to the energy conditions, sulphur's $3d$ orbitals do not in practice take part in the formation of molecular orbitals.* The twelve valence electrons of the SF_6 molecule are located in four bonding and two nonbonding orbitals:

$$[\sigma_s]^2\,[\sigma_p]^6\,[\sigma^{non}]^4$$

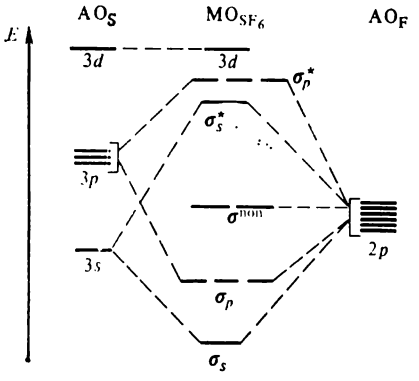


Fig. 138. Energy diagram of the orbitals of the octahedral SF_6 molecule

To explain the structure and properties of p element compounds, the concept of two- and three-centre orbitals is now commonly used. A two-centre two-electron bond is formed by unpaired electrons of the orbital of the central atom (A) and the orbital of the ligand (L). According to the molecular orbital theory, it must be remembered, this corresponds to the formation of two-centre bonding $\Psi_+ \cong \psi_A + \psi_L$ and antibonding $\Psi_- \cong \psi_A - \psi_L$ molecular orbitals. The bonding

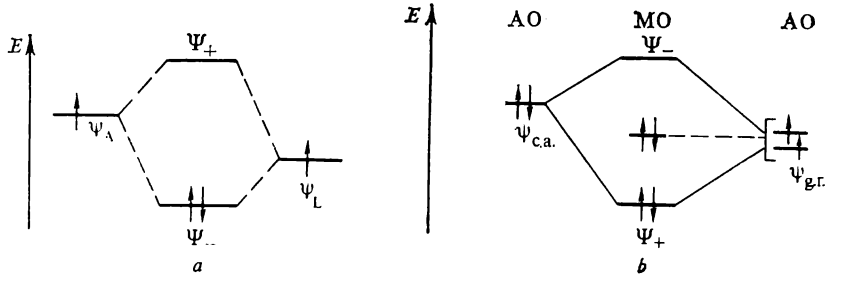


Fig. 139. Diagrams of the molecular orbitals of (*a*) two-centre two-electron and (*b*) a three-centre four-electron interaction

orbital is occupied by an electron pair while the antibonding orbital is vacant (Fig. 139*a*) which explains, for example, the formation of bonds in the molecules

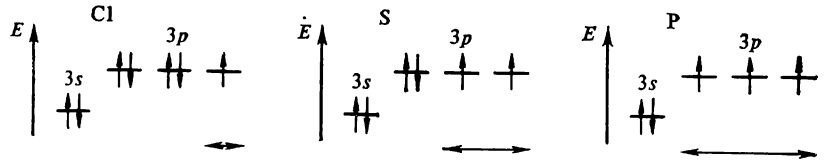
ClF: Cl—F

SF_2: S—F, with F

PF_3: P, with F F F

* See Figs. 212 and 214.

through the involvement of one electron of the chlorine atom, two electrons of sulphur and three electrons of the phosphorus atom:



A three-centre four-electron bond arises through the electron pair of the central atom and two unpaired electrons of two ligands arranged along one line. According to the MO theory this corresponds to the formation of three molecular orbitals, one of which is a three-centre bonding one

$$\Psi_+ \cong \psi_{\text{c.a.}} + \psi_{\text{gr}}$$

and second a two-centre nonbonding orbital

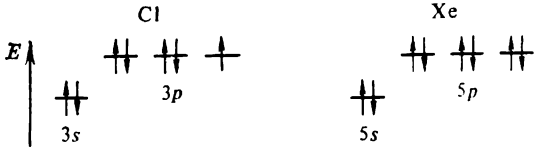
$$\Psi \cong \psi_{\text{gr}}$$

and the third a three-centre antibonding orbital

$$\Psi_- \cong \psi_{\text{c.a.}} - \psi_{\text{gr}}$$

The four electrons of this bond are distributed in the bonding and nonbonding orbitals (Fig. 139*b*), which accounts for the stability of the three-centre four-electron bond.

A three-centre four-electron bond is called *hypervalent*. The concept of hypervalent bond is employed to explain the structure and formation of compounds in which the coordination number of *p* elements (V-VIII groups) is higher than the number of its unpaired electrons. For example, ClF_3 and ClF_5; XeF_2, XeF_4, and XeF_6 compounds are known for chlorine and xenon while chlorine has only one unpaired electron and xenon has none at all:



Consider the molecule of chlorine trifluoride. According to the above concept, one bond is a two-centre two-electron one (as in ClF) while the other is a three-centre four-electron one. The chlorine atom donates one of its 3*p* electron pairs for the formation of this

bond. Since p orbitals are mutually perpendicular in the atom, the ClF_3 molecule has a T-shape configuration (Fig. 140).

Because of the mutual repulsion of electrons the bond angle FClF is therefore a little less than 90°. With two-centre interaction, the Cl—F distance is shorter (0.160 nm) than with three-centre one (0.170 nm). Understandably, the ClF bonds are stronger with a two-centre interaction (250.9 kJ/mol) than with the three-centre one (173.7 kJ/mol).

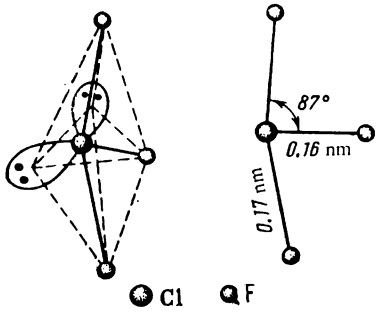


Fig. 140. Structure of the ClF_3 molecule

The spatial configuration of the ClF_3 molecule accords fully with the model of localised electron pairs (see Table 7). Three electron pairs of the ClF_3 molecule are involved in the bond (one pair through a two-centre interaction and two through a three-centre interaction), while two pairs remain unshared in the chlorine atom. The mutual repulsion of five electron pairs accounts for their location at the apexes of a trigonal bipyramid (see Fig. 51).

By a similar argument it can be shown that the ClF_5 molecule is formed by one covalent and two hypervalent bonds. The molecule is a square pyramid (see Fig. 51).

Four-electron three-centre bonds are weaker than two-electron two-centre ones, which is due to the mutual repulsion of the electron pairs.

The formation of a hypervalent bond corresponds to a shift of electron density from the central atom (donor) to the ligands (acceptor) (see Fig. 139*b*). The more electronegative atoms like fluorine or oxygen are therefore the most effective ligands, which also explains the stabilisation of the highest oxidation states of the elements in their fluorine and oxy compounds.

A hypervalent bond will obviously be stronger in those molecules (compared with similar ones) in which the central (donor) atom has a lower ionisation potential. It will be clear from that why, for example, there is a tetrafluoride SF_4 and even a hexafluoride SF_6 for sulphur but no such compounds for oxygen. The ionisation energy of oxygen is so high (13.6 eV) that even fluorine is ineffective as a ligand in the formation of a hypervalent bond. The absence of a pentafluoride for nitrogen (though a rather stable PF_5 is known for phosphorus) can be explained in the same way.

Another characteristic feature of second period elements needs to be mentioned: they form $p\pi - p\pi$ bonds though this type of orbital overlapping is not characteristic of elements of the third and subsequent periods, because the probability of an overlapping of dumbbell p orbitals through their sides falls steeply with increase in the atom's size (Fig. 141). Because of the stability of the $p\pi - p\pi$

bonds, triangular CO_3^{2-} and NO_3^- anions are characteristic of carbon and nitrogen while tetrahedral SiO_4^{4-} and PO_4^{3-} anions, of carbon and phosphorus.

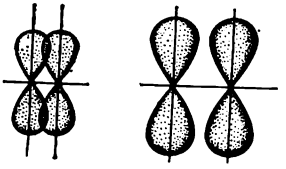


Fig. 141. Effect of internuclear distance on $p\pi$—$p\pi$ overlapping

Ionic compounds are mainly characteristic of *s* elements of groups I and II (the ionisation energy of the atoms being low). The coordination numbers of their ions are high (6, 8) and depend on the size ratio of the ions in the ionic crystals (see Fig. 57).

CHAPTER 2

Hydrogen

The relative simplicity of the atomic structure of hydrogen ($1s^1$) does not mean, of course, that its chemistry is the simplest. On the contrary, it differs in many respects from that of all other elements.

The main peculiarity of hydrogen is that, in contrast to the other elements (except helium), its valence electron is directly in the sphere of action of the nucleus; there is no intermediate electron shell. The positive hydrogen ion H^+ is an elementary particle, the proton.

The peculiarity of structure of the hydrogen atom's electron shell (and of helium) makes it difficult to decide what group of the periodic system to put hydrogen in. In fact, if the number of its valence electrons is taken, it should be assigned to Group I, which is also supported by the similarity of the spectra of the alkali metals and hydrogen. Its ability to give a hydrated unipositive ion H^+(sol) in solution also indicates its similarity to the alkali metals. But in the state of a free ion H^+ (g), the proton, it has nothing in common with the ions of the alkali metals. Furthermore, its ionisation energy is much higher than those of the atoms of the alkali metals.

If, however, we consider the fact that hydrogen needs only one electron to complete its outer layer, it can be put in group VII. Moreover, like the halogen atoms, the hydrogen atom has a high ionisation energy. Many chemists, therefore, put it in group VII. At the same time, it is a special element, and it is largely conventional what group it is put in.

The ionisation energy of the hydrogen atom (13.6 eV, 1312 kJ/mol) is so high that hydrogen(I) compounds with such strong oxidants as

fluorine or oxygen cannot be ionic. If we were to assume the formation of H^+ ions in compounds, their extraordinary polarising action would give rise to covalent bonds. For the same reason the H^+ ion cannot exist in a free state in ordinary chemical phenomena. The specific features of the hydrogen atom's structure accounts for the special type of chemical bond (inherent in hydrogen(I) compounds alone), namely, the *hydrogen bond.*

The formation of a negative hydrogen ion H^- from its atom is an exothermic process (electron affinity, 0.75 eV) and ionic compounds are therefore possible for hydrogen with an oxidation state of —1.

Hydrogen is thus a nonmetallic element. In compounds its oxidation state can be —1 and +1. As with the halogens, ionic compounds are characteristic in which hydrogen acts as a simple anion H^-. In the positive oxidation state, hydrogen forms only covalent compounds and can be a complexing agent in anion complexes.

Hydrogen is very common in nature. Its content of the Earth's crust (atmosphere, lithosphere, and hydrosphere) is 3.0 mole per cent. It is a constituent of water, clays, brown coals, petroleum, etc., and of all animal and vegetable organisms. It is very seldom found in the free state (in volcanic and other natural gases). Hydrogen is the most abundant element in the Universe, constituting about half the mass of the Sun and of most stars. The giant planets of the solar system, Jupiter and Saturn, consist mainly of it. It is present in the atmosphere of several planets and in comets, nebulae, and interstellar gas.

Hydrogen has three isotopes with mass numbers 1, 2, and 3:

^1H	$^2D(^2H)$	$^3T(^3H)$
(p)e	(p+n)e	(p+2n)e
Protium	Deuterium	Tritium

Protium and deuterium are stable isotopes. The normal isotopic composition of natural hydrogen compounds corresponds to the ratio D : H = 1 : 6800 (by the number of atoms). Tritium is beta-radioactive with a half-life of 12.26 years:

$$^3_1T = ^3_2He + \beta^-$$

It is supposed that this reaction is the main source of the ^3_2He isotope in the atmosphere. The content of tritium in atmospheric hydrogen is 4×10^{-15} mole per cent and in atmospheric precipitation about 3×10^{-18} mole per cent. It is probably formed as a result of nuclear reactions induced by cosmic rays. Tritium can be obtained artificially as follows $^6Li\ (n, \alpha)^3T$.*

* The abbreviated way of writing a nuclear reaction is as follows: the bombarding particle and the particle obtained in the reaction are written first and enclosed in parentheses; the symbol of the parent nucleus with its indices is then written to the left of the parentheses and the symbol of the resultant nucleus with its indices on the right.

Simple substances. Having one electron, hydrogen forms only diatomic molecules with the electronic configuration in the ground state $[\sigma_s]^2$. Depending on its isotopic composition the following simple substances are possible: light hydrogen or protium H_2, heavy hydrogen or deuterium D_2, tritium T_2, protodeuterium HD, prototritium HT, and deuterotritium DT.

The molecules of hydrogen are distinguished by great stability, low polarisability, minute size and small mass, and consequently also by high mobility. It therefore has a very low melting point (—259.1 °C) and boiling point (—252.6 °C), second only to helium in this respect. For the same reasons it is barely soluble in water and organic solvents. Solid hydrogen has a hexagonal molecular lattice. Because of its high dissociation energy (435 kJ/mol) the H_2 molecule only breaks down into atoms to any appreciable extent at temperatures above 2000 °C.

Theory suggests that hydrogen should pass into the metallic state at immense pressures. At a pressure of 2×10^{11} Pa at normal temperature molecular hydrogen should be converted into atomic hydrogen. In these conditions, according to theory, the crystal lattice of hydrogen would have protons at the lattice points, while the electrons would be shared; such a crystal would have the conductivity of a metal.

Hydrogen displays both reducing and oxidising properties. In ordinary conditions, because of the stability of its molecules, it is comparatively inactive and reacts directly only with fluorine. But when heated it reacts with many nonmetals (e.g. chlorine, bromine, oxygen, etc.). Its reducing properties are employed to obtain certain simple substances from their oxides and halides:

$$CuO + \overset{0}{H}_2 = Cu + \overset{+1}{H}_2O$$

As an oxidant, hydrogen interacts with active metals

$$2Na + \overset{0}{H}_2 = 2Na\overset{-1}{H}$$

In industry hydrogen is produced mainly from natural and casinghead gases, products of gasifying fuels (water and vapour-air gases) and coke-oven gas. The methods used employ catalytic reactions of the appropriate hydrocarbons (mainly methane) and carbon monoxide with water steam, e.g.

$$CH_4 + H_2O \overset{800\ ^\circ C}{\rightleftharpoons} CO + 3H_2, \quad \Delta H^\circ_{623} = 206\ kJ$$

$$CO + H_2O \overset{600\ ^\circ C}{\rightleftharpoons} CO_2 + H_2, \quad \Delta H^\circ_{298} = -41\ kJ$$

Hydrogen is also produced by incomplete oxidation of hydrocarbons, e.g.

$$2CH_4 + O_2 = 2CO + 4H_2, \quad \Delta H^\circ_{298} = -71\ kJ$$

Since reserves of natural hydrocarbons are decreasing the method of obtaining hydrogen by reducing steam over incandescent coal, forming *producer* gas, is of interest:

$$C + H_2O = CO + H_2, \quad \Delta H^\circ_{298} = 131 \text{ kJ}$$

The energy expended on obtaining it can be compensated by the incomplete oxidation of coal:

$$2C + O_2 = 2CO, \quad \Delta H^\circ_{298} = -221 \text{ kJ}$$

By combining these two processes *water gas*, consisting mainly of H_2 and CO, is obtained. Hydrogen is separated from the mixtures rich in it by deep freezing.

Hydrogen is also produced by the electrolysis of water. In the laboratory it is obtained from the interaction of zinc and hydrochloric or sulphuric acid.

Hydrogen is widely employed in chemical industries to synthesise ammonia, methanol, and hydrogen chloride, to hydrogenate heavy solid and liquid fuels, fats, etc. Mixed with CO (in the form of water gas) it is used as a fuel. The high temperature at which it burns in oxygen (2600 °C) is utilised for welding and cutting refractory metals, quartz, etc. Solid hydrogen is used as one of the most efficient jet fuels. The hydrogen isotopes, tritium and deuterium, are of major importance in nuclear power engineering for moderating nuclear reactions.

The problem of utilising hydrogen has now become especially important. The energy crisis, the problem of environmental protection against the continuing menacing pollution by oil and the combustion products of organic fuels have stimulated mounting interest in hydrogen as an 'ecologically safe' fuel. Hydrogen is the basis of the chemical technology and power engineering of tomorrow.

Compounds of hydrogen in the −1 oxidation state. Depending on the nature of the elements bound with it, hydrogen atoms may be polarised in compounds either positively (o. s. +1) or negatively (o. s. −1) [o. s. means oxidation state]:

LiH	BeH_2	B_2H_6	CH_4	H_3N	H_2O	HF
NaH	MgH_2	AlH_3	SiH_4	H_3P	H_2S	HCl
KH	CaH_2	GaH_3	GeH_4	AsH_3	H_2Se	HBr
RbH	SrH_2	InH_3	SnH_4	SbH_3	H_2Te	HI
CsH	BaH_2					
−1 H compounds			Intermediate compounds		+1 H compounds	

In addition, there is a group of compounds in which the E—H bond is close to nonpolar. In the appropriate conditions they can be regarded as derivatives of $\overset{+1}{H}$ and $\overset{-1}{H}$.

When hydrogen acts as an oxidant it behaves like a typical halogen, forming *hydrides* similar to halides. The formation of the ion H^- from H_2 molecule, however, is an endothermic process (the enthalpy of formation of H^- being $\Delta H^\circ_{f,298} = 150.6$ kJ/mol):

$$\begin{array}{ll} 1/2\ H_2(g) = H(g), & \Delta H^\circ_{298} = 217.5\ \text{kJ} \\ H(g) + e = H^-(g), & \Delta H^\circ_{298} = -66.9\ \text{kJ} \\ \hline 1/2\ H_2(g) + e = H^-(g), & \Delta H^\circ_{298} = 150.6\ \text{kJ} \end{array}$$

The oxidising activity of hydrogen is therefore much weaker than that of the halogens. For the same reason, a marked ionic character is only observed with hydrides of the most active metals, like the alkali and alkaline earth metals, e.g. KH and CaH_2.

These ionic hydrides are white crystalline substances melting at high temperature (i.e. salts). Their melts are characterised by high electrical conductivity; during electrolysis hydrogen is liberated at the anode. Hydrides of Group I *s* elements, like most of their halides, have a NaCl type structure. Chemically ionic hydrides behave like basic compounds.

Hydrides of nonmetals that are less electronegative than hydrogen itself are covalent compounds, e.g. SiH_4 and BH_3. By chemical nature, the hydrides of nonmetals are acidic compounds.

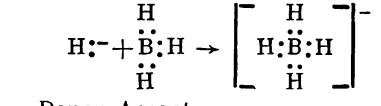
The difference in the chemical nature of hydrides can easily be established by their behaviour during hydrolysis, a characterised feature of which is the liberation of hydrogen. The mechanism of the reaction is that of the oxidation-reduction process. The negatively polarised hydrogen atom $\overset{-1}{H}$ of the hydride and the positively polarised atom $\overset{+1}{H}$ of water pass to a zero oxidation state:

$$\underset{\text{Basic}}{\overset{-1}{K}\overset{+1}{H} + \overset{+1}{H}OH = KOH + \overset{0}{H_2};} \qquad \underset{\text{Acidic}}{\overset{-1}{Si}H_4 + 3\overset{+1}{H}OH = H_2SiO_3 + 4\overset{0}{H_2}}$$

Because hydrogen is liberated, hydrolysis proceeds completely and irreversibly ($\Delta H < 0$, $\Delta S > 0$), the basic hydrides forming alkalis and the acidic ones yielding acids.

The difference between acidic and basic hydrides is very marked when they interact:

$$\underset{\substack{\text{Basic} \\ \text{Donor}}}{LiH} + \underset{\substack{\text{Acidic} \\ \text{Acceptor}}}{BH_3} = \underset{\substack{\text{Lithium} \\ \text{tetrahydride} \\ \text{borate}}}{Li[BH_4]}$$



Their reaction can only proceed, of course, in nonaqueous media (e.g. ether). Lithium hydride, in giving up H^- ions to the complex behaves as a donor of electron pairs, while the BH_3, which accepts the hydride ions, acts as an acceptor.

Aluminium hydride AlH_3 can be regarded as an amphoteric compound. Depending on its partner in the reaction, it may act either as the donor of electron pairs (basic compound) or as the acceptor (acidic compound):

$$AlH_3 + 3BH_3 = Al[BH_4]_3$$

Basic — Aluminium tetrahydride borate (mixed hydride)

$$KH + AlH_3 = K[AlH_4]$$

Acidic — Potassium tetrahydride aluminate

The standard oxidation-reduction potential of the $1/2\ H_2/H^-$ pair is -2.23 V. The H^- ion is consequently one of the strongest reducing agents; ionic and complex hydrides are therefore strong reducing

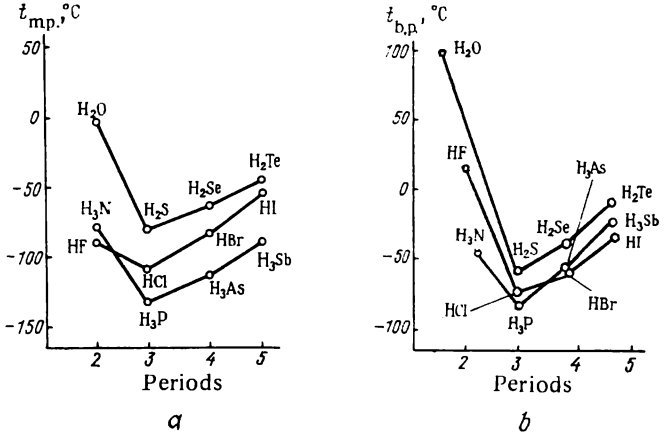


Fig. 142. (*a*) Melting points and (*b*) boiling points of hydrogen compounds of Group VII, VI, and V *p* elements

agents. They are widely employed in various types of synthesis, to obtain hydrogen, and in chemical analysis. Calcium hydride CaH_2 is also employed as a dehydrating agent to remove traces of moisture.

Compounds of hydrogen(I). A positive polarisation of hydrogen atoms is observed in its numerous covalent compounds. In normal conditions these are gases (HCl, H_2S, H_3N), liquids (H_2O, HF, HNO_3), or solids (H_3PO_4, H_3BO_3). Their properties greatly depend on the

nature of the element with which the hydrogen is directly bound. A hydrogen bond is particularly characteristic, for instance, of compounds containing F—H, O—H, and N—H bonds, so that HF, H_2O, and H_3N have anomalously high melting and boiling points compared with similar binary compounds of hydrogen with other elements of this group (Fig. 142). The slope of the curves describing the enthalpies of evaporation of these compounds is similar.

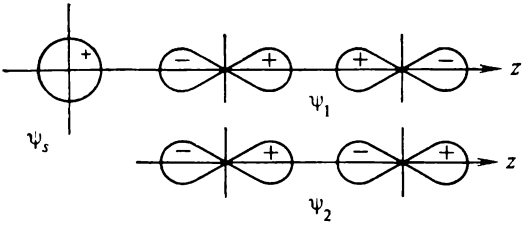
Because of their capacity to form hydrogen bonds and to enter into donor-acceptor interactions, liquid HF, H_2O, and H_3N are good ionising solvents (see p. 139).

The tendency inherent in hydrogen to form anion complexes, or *hydrogenates*, is realised, for example, in the following reactions:

$$KF + HF = K[HF_2], \quad KNO_3 + HNO_3 = K[H(NO_3)_2]$$

Potassium difluorohydrogenate — Potassium dinitrohydrogenate

Hydrogenate complexes are formed through the hydrogen bond: $[F\cdots H\cdots F]^-$; $[O_2NO\cdots H\cdots ONO_2]^-$. Their structure is linear. Their formation can be explained as follows. The orbitals of HF_2^- arise through a linear combination of the orbitals of the central atom φ_s (1*s* orbital of H) and the group orbitals of the peripheral atoms φ_1, φ_2 ($2p_z$ orbitals of two fluorine atoms):



By symmetry conditions, the combination of ψ_s and ψ_1 orbitals results in the formation of bonding σ_s and antibonding σ_s^* molecular orbitals of the HF_2^- ion (see Fig. 143):

$$\Psi(\sigma_s) \sim \psi_s + \psi_1,$$
$$\Psi(\sigma_s^*) \sim \psi_s - \psi_1$$

There being no suitable orbital of the central atom (with respect to symmetry conditions) for the group orbital ψ_2, the ψ_2 orbital of HF_2^- is therefore nonbonding (Fig. 143). Four electrons (one electron of the hydrogen atom, two of the two fluorine atoms, and one of the ion charge) are distributed in the bonding σ and nonbonding σ^{non} molecular orbitals. The presence of electrons in the molecular σ

nonbonding orbital corresponds to a concentration of surplus negative charge on the terminal atoms. Hydrogenate ions of the HX_2^- type should consequently be most stable when X is the most elec-

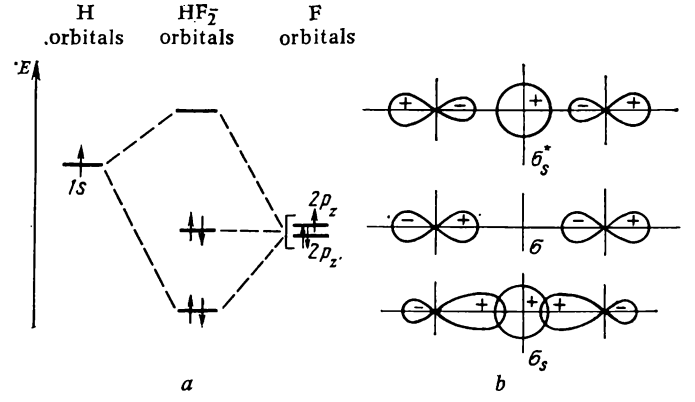
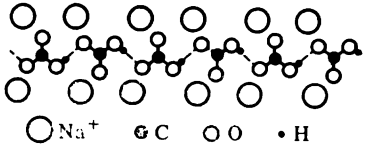


Fig. 143. (*a*) Energy diagram of the orbitals of an HF_2^- ion and (*b*) a scheme of their formation

tronegative atom or group of atoms. In the HF_2^- ion, for example, the bond is almost three times as strong as the intermolecular hydrogen bond (see p. 99).

Most hydrogenates can only exist in nonaqueous or saturated aqueous solutions, and also in the solid state.

Hydrogen atoms are also constituents of acid salts of the NaHS, $NaHCO_3$, and $NaHSO_4$ type. The HS^-, HCO_3^-, and HSO_4^- groups can exist in solution as free ions and are then known respectively as *hydrosulphide*, *hydrocarbonate* (*bicarbonate*), and *hydrosulphate* (*bisulphate*) ions. The structure of acid salts in the solid state is also determined by the hydrogen bond. The structural diagram of sodium bicarbonate $NaHCO_3$ is shown below:



Hydrogen compounds with metals. Hydrogen compounds of *d* and *f* elements have metallic properties. These compounds are obtained as dark, metal-like powders or a brittle mass; their electrical and heat conductivity are typical of metals. They are hydrides of a nonstoichiometric composition. The idealised composition of metal hydrides generally corresponds to the formulas MH (VH, NbH, TaH), MH_2 (TiH_2, ZrH_2, HfH_2, ScH_2), and MH_3 (UH_3, PaH_3).

There are two theories of the character of the bonds in hydrides of *d* and *f* elements. According to one hydrogen enters the lattice as an H^+ ion and gives up its electron to the conduction band of the metallic structure. According to the other, the hydrogen atoms capture electrons from the conduction band and are present in the crystal lattice as hydride H^- ions. It can be supposed that there is a gradual transition in the periodic system (from Group I to Group V) from ionic hydrides (salt type) to hydrides in which the hydrogen is in the H^+ form.

The first three metals of each family of *d* elements (i.e. Sc, Ti and V; Y, Zr and Nb; La, Hf and Ta), it should be noted, absorb hydrogen with a considerable exothermic effect. The enthalpies of formation of some hydrides, for example, are as follows:

	ScH_2	YH_2	LaH_2	TiH_2	ZrH_2
$\Delta H^\circ_{f,298}$, kJ/mol	—69	—186	—208	—144	—169

Group VI, VII, and VIII *d* metals are only slightly active in relation to hydrogen. The enthalpy of formation of FeH_2 is only —0.84 kJ/mol. Palladium is an exception; it absorbs hydrogen very actively, which is probably connected with its unique electronic configuration ($4d^{10}$; a 'gap' of two 5*s* electrons).

Hydrides are formed by simple substances with lowered entropy, since the initial substances are a gas and solid, and the end product a solid. Those compounds can only therefore be synthesised directly from hydrogen and the metals that are formed with the liberation of much heat. Otherwise hydrides of *d* and *f* elements can only be obtained indirectly.

Metallic hydrides are used as reducing agents in electric plating and to obtain the metals in the form of a powder. In this case, Ti or V, for example, is saturated with hydrogen, the brittle hydride formed is ground to a powder, and heated *in vacuo* to obtain the powdered metal. The pure metals are plastic so that it is impossible to powder them by simple grinding. Hydrides are also used in hydration reactions and to synthesise many compounds of *d* and *f* elements. Titanium hydride is of special interest as a 'reservoir' of hydrogen.

CHAPTER 3

Group VII *p* Elements

The main subgroup of Group VII comprises fluorine F, chlorine Cl, bromine Br, iodine I, and astatine At:

F $1s^22s^22p^5$

Cl $2s^22p^63s^23p^5$

Br $3s^23p^63d^{10}4s^24p^5$

I $4s^24p^64d^{10}5s^25p^5$

At $4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^5$

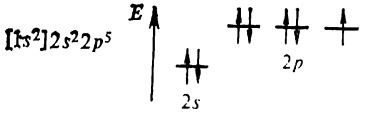
By their electron configuration (similar structure of the outer and penultimate electron layers) bromine, iodine, and astatine form a bromine subgroup; fluorine and chlorine are typical elements. The main constants of *p* elements of Group VII and also hydrogen are:

	$_1$H	$_9$F	$_{17}$Cl	$_{35}$Br	$_{53}$I	$_{85}$At
Valence electrons	$1s^1$	$2s^22p^5$	$3s^23p^5$	$4s^24p^5$	$5s^25p^5$	$6s^26p^5$
Atomic mass	1.008	18.988	35.453	79.904	126.904	[210]
Covalent radius of atom, nm	—	0.064	0.099	0.114	0.133	—
Ionic radius E^-, nm	0.136	0.133	0.181	0.196	0.220	0.23
Conventional E^{7+} ion radius, nm	—	—	0.026	0.039	0.050	0.062
Electron affinity, eV	0.75	3.5	3.6	3.5	3.3	—
Ionisation energy, eV ($E \rightarrow E^+$)	13.6	17.42	12.97	11.84	10.45	9.2
Abundance, mole per cent	3.0	2.8×10^{-2}	2.6×10^{-2}	8.5×10^{-5}	4×10^{-6}	Traces

As will be seen the atomic radius increases in the series F—Cl—Br—I—At while the ionisation energy decreases. This indicates a weakening of the elements' nonmetallic character: fluorine is the most characteristic nonmetal element, but astatine has certain characteristics of metals.

3.1. Fluorine

In the ground state fluorine has the following electron configuration:



The presence of one unpaired electron determines its similarity to hydrogen, but the difference in the total number of valence electrons and orbitals accounts for the significant difference between them. The oxidation state of fluorine, the most electronegative element (4.0), is taken as —1. Its maximum valence, as with other second period elements, is four.

Fluorine is a quite common element, and constitutes about 0.03 mole per cent of the Earth's crust. The most important fluorine minerals are *fluorspar* CaF_2, *cryolite* Na_3AlF_6, and *fluorapatite* $Ca_5(PO_4)_3F$. There are fluorine compounds in the human body (mainly in the teeth and bones). Only one isotope of fluorine, ^{19}F, occurs in nature; unstable isotopes with mass numbers from 16 to 21 have been obtained artificially.

The simple substance. Like hydrogen, fluorine forms a diatomic molecule F_2 which corresponds to the following electron configuration:

$$[\sigma_s]^2\,[\sigma_s^*]^2\,[\sigma_z]^2\,[\pi_{x,y}]^4\,[\pi_{x,y}^*]^4$$

Since the bonding orbitals contain two surplus electrons compared with the number in the antibonding orbitals, the order of the bond in the F_2 molecule is taken as unity

The fluorine molecule F_2 has a relatively small mass and is quite mobile. In normal conditions fluorine is therefore a pale yellow gas. Its melting point is —223 °C and boiling point —187 °C.

Fluorine is extraordinarily active chemically, and is a powerful oxidising agent. Its high chemical activity is due to the low dissociation energy of its molecule (159 kJ/mol); at the same time the chemical bond in most fluorine compounds is very strong (about 200-600 kJ/mol). The activation energy of reactions with fluorine atoms, moreover, is low ($\leqslant$4 kJ/mol). Fersmau characterised it as 'omnivorous' since even such stable substancer as glass wool and water burn in a fluorine atmosphere:

$$SiO_2 + 2F_2 = SiF_4 + O_2, \quad 2H_2O + 2F_2 = 4HF + O_2$$

In these reactions oxygen (!) is formed as a combustion product, i.e. fluorine is a stronger oxidising agent than oxygen.

Fluorine's interaction with most simple substances is exceptionally vigorous. It reacts with sulphur and phosphorus at temperatures as low as that of liquid air (—190 °C):

$$S + 3F_2 = SF_6, \quad \Delta H^\circ_{298} = -1207 \text{ kJ}$$

$$2P + 5F_2 = 2PF_5, \quad \Delta H^\circ_{298} = -3186 \text{ kJ}$$

Fluorine oxidises some of the 'inert' gases:

$$Xe + 2F_2 = XeF_4, \quad \Delta H^\circ_{298} = -252 \text{ kJ}$$

Only helium, neon, and argon do not react directly with it.

Because of its high chemical activity fluorine corrodes almost all materials. The apparatus for obtaining, storing, and transporting it are therefore made of nickel (and certain of its alloys), which is fluorine-resistant because of the formation of a protective film of NiF_2. The problem of transporting fluorine has now been solved, and it is carried in bulk in big road tankers.

Because of its high oxidising power, and the high stability of its compounds, fluorine is obtained in the free state by electrolysis of its molten compounds. A eutectic mixture HF—KF or potassium fluorohydrogenates is normally used for the purpose.

Fluorine began to be widely used in connection with work on the diffusion separation of uranium isotopes (in the form of $^{235}UF_6$ and $^{238}UF_6$). It is now commonly used to synthesise various refrigerants and fluoroplastic polymers of high chemical stability. Liquid fluorine and some of its compounds are used as oxidants in rocket fuels.

Compounds of fluorine (o.s.—1). The properties of fluorides change in accordance with the regular change in the properties of elements in the periods and groups of the periodic system, for example,

	$\underline{NaF \quad MgF_2}$	AlF_3	$\underline{SiF_4 \; PF_5 \; SF_6 \; (ClF_5)}$
Chemical nature	basic	amphoteric	acidic
Anion complexes	— —	AlF_6^{3-}	SiF_6^{2-} PF_6^- SF_6^0 (ClF_6^-)

Ionic fluorides are crystalline substances melting at high temperatures. The coordination number of the fluoride ion is six (NaF) or four (CaF_2). Covalent fluorides are gases or liquids.

Fluorides with a high polarity of bonds occupy an intermediate position between ionic and covalent fluorides, and can be called ionic-covalent compounds. Examples are crystalline ZnF_2, MnF_2, CoF_2, NiF_2, in which the effective charges of the electropositive atoms are 1.56, 1.63, 1.46, and 1.40 respectively.

Many fluorides of metals with low oxidation states are obtained through the action of a solution of HF on oxides, hydroxides, carbonates, etc., e.g.

$$3HF + Al(OH)_3 = AlF_3 + 3H_2O$$

The fluorides of nonmetals and metals with high oxidation states are obtained through the fluorination of the simple substances or low fluorides, e.g.

$$ClF + F_2 = ClF_3$$

Most crystalline fluorides are insoluble in water. Only fluorides of Group I *s* elements (except LiF), and AgF, HgF_2, SnF_2, and certain others are readily soluble in water.

In chemical nature ionic fluorides are basic compounds and covalent fluorides acidic. For example, in the reaction

$$\underset{\text{Basic}}{2NaF} + \underset{\text{Acidic}}{SiF_4} = \underset{\substack{\text{Sodium}\\ \text{hexafluorosilicate}}}{Na_2[SiF_6]}$$

the ionic fluoride NaF acts as a donor of electron pairs and the covalent fluoride SiF_4 as an acceptor of the pairs donated by the fluoride ion. As the acidic character of fluorides increases, for example, in the series MgF_2—AlF_3—SiF_4, their interaction with basic fluorides has an increasing negative value of ΔG°:

$$NaF\ (c) + MgF_2\ (c) = NaMgF_3\ (c), \qquad \Delta G^\circ_{298} = -14\ kJ$$
$$NaF\ (c) + 1/3\ AlF_3\ (c) = 1/3\ Na_3AlF_6\ (c), \qquad \Delta G^\circ_{298} = -26\ kJ$$
$$NaF\ (c) + 1/2\ SiF_4\ (g) = 1/2\ Na_2SiF_6\ (c), \qquad \Delta G^\circ_{298} = -51\ kJ$$

During hydrolysis basic fluorides create an alkaline medium and acidic ones an acid medium:

$$\underset{\text{Acidic}}{SiF_4} + 3H_2O = H_2SiO_3 + 4HF$$

Amphoteric fluorides react with both acidic and basic fluorides, forming mixed fluorides in the latter case, e.g.

$$\underset{\substack{\text{As an}\\ \text{acidic}\\ \text{compound}}}{2KF} + BeF_2 = K_2[BeF_4]$$

$$\underset{\substack{\text{As a basic}\\ \text{compound}}}{BeF_2} + \underset{\substack{\text{Mixed}\\ \text{fluoride}}}{SiF_4 = Be[SiF_6]}$$

Complex fluorides are extremely varied (see, for example, Table 30). The coordination number of second period elements is four in relation to fluorine and six for elements of the other periods. In addition, there are complex fluorides in which the coordination number of the complexing agent is seven, eight, or nine: for example,

$$K_2[BeF_4] \quad K_3[AlF_6] \quad K_2[NbF_7] \quad K_2[WF_8] \quad K_2[ReF_9]$$

These examples also show that the highest oxidation state of the central atoms is stabilised in fluoride complexes.

The derivatives of fluoride complexes are predominantly ionic or belong to the mixed (polymeric) fluorides (e.g. $BeSiF_6$). Fluorine compounds with hydrogen of the type HBF_4, HPF_6, and H_2SiF_6 are unstable in the free state; their aqueous solutions are very strong acids.

The molecule of hydrogen fluoride HF is strongly polar ($\mu = 0.64 \times 10^{-29}$ C·m, $\delta_H = 0.4 +$, $\delta_F = 0.4 -$). Its molecules have a strong tendency to associate in zig-zag chains because of the hydrogen bonds (see p. 99). In normal conditions, therefore, hydrogen fluoride is a colourless liquid freezing at −83 °C and boiling at +19.5 °C. It has a pungent odour, and fumes in air. Even in the

gaseous state it is a mixture of polymers H_2F_2, H_3F_3, H_4F_4, H_5F_5, and H_6F_6. Simple HF molecules can only exist at temperatures above 90 °C. Because of the high strength of the bond (dissociation energy, 565 kJ/mol) thermal decomposition of HF into atoms becomes appreciable only at temperatures above 3500 °C.

Hydrogen fluoride is usually obtained by the action of sulphuric acid on fluorspar:

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

The ionisation proper of liquid HF is insignificant ($K = 2.07 \times \times 10^{-11}$). It occurs through the transfer of a proton (or fluoride ion) from one molecule to another with subsequent transformation of the intermolecular hydrogen bond into interatomic and covalent bonds. Solvated *fluoronium* FH_2^+ and *fluorohydrogenate* HF_2^- ions are produced as a result:

$$H—F \cdots H—F \cdots H—F \rightleftarrows [H—F—H]^+ + [F \cdots H \cdots F]^-$$

or

$$HF \cdots HF \cdots HF \rightleftarrows FH_2^+ + HF_2^-$$

Liquid hydrogen fluoride is a strong ionising solvent.

It readily dissolves water and fluorides, sulphates and nitrates of Group I *s* elements, and rather less readily similar compounds of Group II *s* elements. During dissolution, the solutes accept protons from the HF molecules to increase the concentration of negative ions (HF_2^-), i.e. behave as bases: for example,

$$KNO_3 + 2HF \rightleftarrows K^+ + HNO_3 + HF_2^-$$

As was said above (p 140), even HNO_3 behaves as a base in these conditions:

$$HNO_3 + 2HF \rightleftarrows NO_3H_2^+ + HF_2^-$$

while ethyl alcohol, which is indifferent in water, becomes as strong a base in liquid hydrogen fluoride as KOH is in water:

$$C_2H_5OH + 2HF \rightleftarrows C_2H_5OH_2^+ + HF_2^-$$

Substances that are acceptors of fluoride ion, like BF_3 or SbF_3, behave as acids in liquid hydrogen fluoride:

$$BF_3 + 2HF = HF_2^+ + BF_4^-$$

$$SbF_5 + 2HF = HF_2^+ + SbF_6^-$$

When acids are dissolved the concentration of positive FH_2^+ fluoride ions increases.

The fluorides of aluminium and chromium(III) are amphoteric compounds in liquid hydrogen fluoride:

$$3NaF + AlF_3 = 3Na^+ + AlF_6^{3-}$$

As an acidic compound

$$AlF_3 + 3BF_3 = Al^{3+} + 3BF_4^-$$

As a basic compound

Hydrogen fluoride is infinitely soluble in water, its molecules being ionised to form OH_3^+ and F^- ions. The latter interact with HF to form fluorohydrogenate ions:

$$HF + H_2O \rightleftarrows OH_3^+ + F^-, \quad K = 7.2 \times 10^{-4}$$
$$HF + F^- \rightleftarrows HF_2^-, \quad K = 5.1$$

or, to sum up

$$2HF + H_2O \rightleftarrows OH_3^+ + HF_2^-$$

A solution of HF (*hydrofluoric acid*) is an acid of medium strength (see p 307). It contains also complex $H_2F_3^-$, $H_3F_4^-$, $H_nF_{n+1}^-$ ions. Therefore, when it is neutralised, fluorohydrogenates of the type $K[HF_2]$ (m.p. 239 °C), $K[H_2F_3]$ (m.p. 62 °C), $K[H_3F_4]$ (m.p. 66 °C), and $K[H_4F_5]$ (m.p. 72 °C), rather than simple fluorides, are formed. These compounds crystallise well as a rule and melt without decomposition. Polymeric hydrogenate ions have a zig-zag configuration, being formed by hydrogen bonding. The thermal decomposition of fluorohydrogenates is used to obtain HF:

$$K[H_nF_{n+1}] = K[H_{n-1}F_n] + HF$$

A characteristic feature of hydrofluoric acid is that it can interact with silicon dioxide

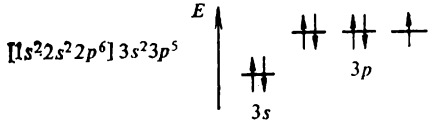
$$SiO_2\ (c) + 4HF\ (sol) = SiF_4\ (g) + 2H_2O\ (l)$$

It is therefore impossible to store the acid in glass containers. Usually it is kept in vessels made of lead, rubber, polyethylene, or wax. The acid is toxic; on the skin it causes burns that are slow to heal.

Hydrofluoric acid is used for etching glass, removing sand from metal castings, preparing fluorides, and so on. Hydrogen fluoride is used mainly in organic synthesis.

3.2. Chlorine

Chlorine is an incomplete electronic analogue of fluorine



Its atom has one unpaired electron, which determines its likeness to hydrogen and fluorine. At the same time, its valence orbitals are larger than those of fluorine, its ionisation energy I is much lower,

its electron affinity F is markedly higher, and its polarisability greater:

	r_{orb}, nm	I, eV	F, eV
F	0.036	17.42	3.45
Cl	0.072	12.97	3.61

Chlorine's maximum coordination number, as with all the other third period p elements, is six.

Being a strongly electronegative element (electronegativity = = 3.0), chlorine has an oxidation state of —1 in most of its compounds, but in compounds with more electronegative fluorine, oxygen, and nitrogen its oxidation state is positive. Chlorine compounds with oxygen are most varied; its oxidation state in them is +1, +3, +5. and +7, and also +4 and +6.

Chlorine is a typical nonmetal. Consequently a tendency to form simple and complex anions in chemical transformations is most typical of it.

Chlorine is one of the relatively abundant elements (0.02 mole per cent). It occurs mainly in the form of *chlorides*, i.e. compounds with the most stable oxidation state of chlorine. Their most important minerals are NaCl (*rock salt*), NaCl·KCl or *sylvinite*, and $KCl \cdot MgCl_2 \cdot 6H_2O$ or *carnallite*. Sea water contains a vast quantity of chlorides. They are also constituents of all living organisms.

Chlorine occurs in natural compounds in the form of its isotopes ^{35}Cl (75.53 per cent) and ^{37}Cl (24.47 per cent). In addition, radioactive isotopes ^{33}Cl, ^{34}Cl, ^{36}Cl, ^{38}Cl, and ^{39}Cl have been obtained artificially.

The simple substance. The molecule of chlorine, like those of hydrogen and fluorine, is diatomic. The dissociation energy of Cl_2 is higher (243 kJ/mol) than that of F_2 (159 kJ/mol). The breakdown of chlorine molecules into atoms becomes appreciable above 1000 °C.

The greater stability of the chlorine molecule Cl_2 (compared with F_2) can be explained by the stronger repulsion of the nonbonding electrons in the fluorine molecule than in the bigger chlorine molecule.

It is supposed that there is additional π bonding in the chlorine molecule (in contrast to H_2 and F_2), which arises through the donor-acceptor mechanism at the expense of an unshared electron pair of one atom and a free 3*d* orbital of the other. The bond order is assumed to be 1.12.

In ordinary conditions chlorine is a yellowish green gas boiling at —34.2 and freezing at —101.0 °C. Its solubility in water is limited (one volume of water dissolving around two volumes of chlorine). When aqueous solutions of chlorine are cooled they precipitate clathrate crystals with an approximate composition of $Cl_2 \cdot 6H_2O$ and $Cl_2 \cdot 8H_2O$.

Chlorine is an active oxidising agent

$$1/2\ Cl_2\ (g) + e^- = Cl^-\ (g), \quad \Delta G^\circ_{298} = -240\ kJ$$
$$1/2\ Cl_2\ (g) + e^- = Cl^-\ (sol), \quad \Delta G^\circ_{298} = -131\ kJ$$

It reacts very energetically with metals and most nonmetals (except O_2, N_2, and inert gases), and readily oxidises many complex compounds. Its reducing properties are displayed only in reaction with fluorine. Chlorine also enters disproportionation reactions, for which an alkaline medium is most favourable, promoting the formation of simple and complex anions

$$Cl_2 + 2OH^- \rightleftharpoons Cl^- + ClO^- + H_2O$$
$$Cl_2 + 2NaOH \rightleftharpoons NaCl + NaClO + H_2O$$

Free chlorine is obtained by oxidising chlorides; in the laboratory it is prepared by chemical oxidation of concentrated hydrochloric acid, and in industry either by electrolysis of an aqueous solution of NaCl or as a by-product in the preparation of sodium by electrolysis of molten NaCl. Chlorine is used for sterilising drinking water. It is widely used as a strong oxidant in various chemical industries. It also has an important role in nonferrous metallurgy (see p. 249).

Compounds of chlorine (o.s. —1). The character of the chemical bond, and hence the properties of chlorides (like fluorides), changes regularly in the groups and periods of the periodic system (see Fig. 130). In the series of chlorides of elements in a given period, for instance, the type of chemical bond changes from a predominantly ionic one in those of typical metals to covalent in those of nonmetals. Ionic chlorides are solid crystalline substances melting at high temperatures, while covalent chlorides are gases, liquids, or low-melting solids. Ionic-covalent chlorides occupy an intermediate position.

Ionic chlorides (the chlorides of metals) have basic properties; covalent chlorides (the chlorides of nonmetals) are acidic compounds:

	NaCl	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_5**	**(SCl_6)**
M. p., °C	800	714	193	—70	159 (subl.)	—
Acid-base properties	Basic		Ampho-teric	Acidic		

Basic chlorides do not hydrolyse; acidic ones hydrolyse completely and irreversibly, forming acids:

$$SiCl_4 + 3HOH = H_2SiO_3 + 4HCl$$

A difference in properties of chlorides of various types is also displayed during their interactions with each other, e.g.

$$\underset{\text{Basic}}{KCl} + \underset{\text{Acidic}}{AlCl_3} = K[AlCl_4]$$

Basic chlorides donate electron pairs (from the chloride ion Cl^-) and acidic chlorides accept them. Amphoteric chlorides react with both acidic and basic compounds.

Most chlorides of metals are readily soluble in water (except AgCl, CuCl, AuCl, TlCl, and $PbCl_2$).

Chlorides are obtained by chlorinating the simple substances with chlorine or dry hydrogen chloride

$$2Fe + 3Cl_2 = 2FeCl_3$$

$$Fe + 2HCl\ (g) = FeCl_2 + H_2$$

from the interaction of oxides with chlorides (often CCl_4), or from chlorine in the presence of coal

$$TiO_2 + 2Cl_2 + C = TiCl_4 + CO_2$$

Hydrogen chloride HCl is of great industrial value. In ordinary conditions it is a colourless gas with a boiling point of —84.9 °C and freezing point of —114.2 °C. It is synthesised in industry from the simple substances:

$$H_2\ (g) + Cl_2\ (g) = 2HCl\ (g), \quad \Delta G^\circ_{298} = -190\ kJ$$

Hydrogen chloride is absorbed very well by water, one volume of H_2O taking up about 450 volumes of HCl at 20 °C. An aqueous solution of HCl is a strong acid ($pK_a = -9.1$) known as *hydrochloric* acid. Being strong, it is widely used in industry, medicine, the laboratory, etc.

Chlorides display their reducing properties in reactions with strong oxidants, and during electrolysis. Concentrated hydrochloric acid, for instance, acts as a reductant in reaction with manganese(IV) oxide

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

the reaction that is used to obtain chlorine in the laboratory.

When heated hydrogen chloride is oxidised by oxygen (over $CuCl_2$ as a catalyst)

$$4HCl\ (g) + O_2\ (g) = 2H_2O\ (g) + 2Cl_2\ (g)$$

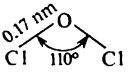
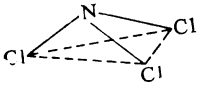
The reaction is accompanied with a decrease in the system's entropy, so that, in accordance with $\Delta G = \Delta H - T\,\Delta S$, its ΔG becomes positive with rising temperature and the process proceeds from right to left. This example illustrates the relativity of our concept of the comparative oxidation-reduction activity of substances. In this case oxygen is a stronger oxidant at moderate temperatures, while chlorine is the oxidant at high temperatures.

Compounds of chlorine (I). An oxidation state +1 of chlorine is observed in the fluoride ClF, oxide Cl_2O, and nitride Cl_3N, and in the corresponding anion complexes $[ClF_2]^-$, $[ClO]^-$, and $[ClN]^{2-}$:

ClF	Cl_2O	Cl_3N
$[ClF^z]^-$	$[ClO]^-$	$[ClN]^{2-}$

A general survey of the binary compounds of chlorine(I) is given in Table 31.

Table 31. **Binary Compounds of Chlorine(I)**

Compounds	Molecular structure	$\mu \times 10^{29}$, C·m	M.p., °C	B.p., °C	State of aggregation in ordinary conditions	ΔH_f°, 298°, kJ/mol	ΔG_f°, 298°, kJ/mol
Fluoride ClF	Dumb-bell	0.22	—154	—101.1	Colourless gas	—50	—51
Oxide Cl_2O	 Angular	0,26	—121	—3.8	Yellow-brown gas	+76	+93
Nitride Cl_3N	 Trigonal pyramidal	—	—27	+71	Dark yellow volatile oil	+230	—

ClF is the sole binary compound of chlorine(I) that is relatively stable, being slightly exothermic. Chlorine monofluoride is formed when dry Cl_2 and F_2 are heated to temperatures above 270 °C. The nitride Cl_3N and oxide Cl_2O are unstable endothermic compounds. The oxide Cl_2O decomposes easily (explosively) into Cl_2 and O_2 when slightly heated, on contact with organic matter, or even during pouring (in the liquid state). The Gibbs' energies of the formation of Cl_2O and Cl_3N are positive, so these compounds are obtained by indirect methods.

The binary compounds of chlorine(I) are acidic as is evident from their reaction with water:

$$Cl_2O + HOH = 2HClO$$

$$ClF + HOH = HClO + HF$$

$$Cl_3N + 3HOH = 3HClO + H_3N$$

Among derivatives of the complex oxychlorate(I) anion $[ClO]^-$, known as *hypochlorites*, the compounds of the alkali and alkaline earth metals are relatively stable. The hypochlorites of these elements are water-soluble salts, obtained by passing chlorine into

cooled alkali solutions

$$2OH^- + Cl_2 \rightleftarrows Cl^- + ClO^- + H_2O$$
$$2KOH + Cl_2 \rightleftarrows KCl + KClO + H_2O$$

Hydrogen oxychlorate(I) HClO is unstable and is known only in the dilute solution as *hypochlorous acid*, which is obtained, together with hydrochloric acid, during hydrolysis of chlorine:

$$Cl_2 + HOH \rightleftarrows H^+ + Cl^- + HClO$$
$$Cl_2 + HOH \rightleftarrows HCl + HClO$$

Hypochlorous acid is weak (see Table 21).

When chlorine is passed into water containing suspended mercuric oxide a solution of HClO is produced:

$$2Cl_2 + H_2O + 2HgO = 2HClO + Hg_2OCl_2$$

The derivatives of chlorine(I) are strong oxidants. ClF is especially aggressive, reacting with substances even more energetically than free fluorine. For that reason it is used as a fluorinating agent. Hypochlorites are used as bleaches. The bleaching effect depends on the oxidation of contaminants by the hypochlorous acid which is displaced from the hypochlorite solutions by carbonic acid:

$$NaClO + H_2O + CO_2 = NaHCO_3 + HClO$$

Compounds of chlorine(I) are susceptible to disproportionation reactions which proceed more easily in hypochlorites

$$3\overset{+1}{K}\overset{}{Cl}\overset{}{O} = 2K\overset{-1}{Cl} + K\overset{+5}{Cl}O_3$$

Oxychlorates(I) decompose readily (in particular, in the presence of catalysts), liberating oxygen

$$2\overset{+1}{K}\overset{-2}{Cl}O = 2K\overset{-1}{Cl} + \overset{0}{O_2}$$

Calcium hypochlorite, $Ca(ClO)_2$, is of the greatest practical importance (as a bleaching agent, an agent for degasification, and a cheap oxidant). It is prepared by reacting chlorine with slaked lime:

$$2Ca(OH)_2 + Cl_2 = Ca(ClO)_2 + CaCl_2 + 2H_2O$$

As will be seen from the reaction equation, $CaCl_2$ is formed along with the $Ca(ClO)_2$. The commercial product obtained (known as *chloride of lime* or *bleaching powder*) can therefore be regarded as a mixed compound, calcium hypochlorite-chloride, $CaCl(ClO)$. The $\overset{+1}{Cl}$ content of chloride of lime is usually determined by the quantity of chlorine liberated during its interaction with hydrochloric acid:

$$Ca\overset{+1}{Cl}(\overset{}{Cl}O) + 2H\overset{-1}{Cl} = CaCl_2 + \overset{0}{Cl_2} + H_2O$$

Crystalline substances of the $\overset{+1}{M}[ClF_2]$ type (where M is an alkali metal) are known among the derivatives of the difluorochlorate(I) complex. They are formed through the interaction of basic fluorides and ClF in nonaqueous solutions (at 175 °C and 10 MPa):

$$MF + ClF = M[ClF_2]$$

Compounds of chlorine(III). A +3 oxidation state of chlorine is displayed in chlorine trifluoride ClF_3, in the tetrafluorochlorate(III) complex $[ClF_4]^-$, and in the dioxychlorate(III) complex $[ClO_2]^-$:

ClF_3	(Cl_2O_3)
$[ClF_4]^-$	$[ClO_2]^-$

Chlorine(III) oxide is not known.

Chlorine trifluoride is a pale greenish gas (f.p. −76.3 °C, b.p. 11.6 °C). It can be obtained by heating ClF in the presence of excess fluorine. It is an acidic compound in nature. Tetrafluorochlorates(III) of potassium, rubidium, and caesium of the $\overset{+}{M}[ClF_4]$ type are formed by the fluorination of MCl or by reacting MF with liquid ClF_3:

$$MCl + 2F_2 = M[ClF_4], \quad MF + ClF_3 = M[ClF_4]$$

Tetrafluorochlorates(III) are solids decomposing at temperatures in the range of 200-300 °C.

Derivatives of the ClO_2^- ion are called *chlorites*. The chlorites of the alkali and alkaline-earth metals are white crystalline substances. Hydrogen dioxychlorate(III), $HClO_2$, has not been obtained in the free state. It decomposes quickly even in an aqueous solution. A solution of $HClO_2$ is an acid of medium strength ($K_a = 1 \times 10^{-2}$), called *chlorous acid*.

Compounds of Cl(III) are strong oxidants, especially ClF_3 and $M[ClF_4]$. Glass wool, Al_2O_3, MgO, and other stable substances will burn in ClF_3 vapour:

$$2Al_2O_3 + 4ClF_3 = 4AlF_3 + 3O_2 + 2Cl_2$$

When heated chlorites are disproportionated

$$3\overset{+3}{NaClO_2} = \overset{-1}{NaCl} + 2\overset{+5}{NaClO_3}$$

and decompose with liberation of oxygen

$$\overset{+3\,-2}{NaClO_2} = \overset{-1}{NaCl} + \overset{0}{O_2}$$

In the presence of organic substances, solid oxychlorates and fluorochlorates(III) explode from a blow.

Chlorine trifluoride and the tetrafluorochlorates(III) are employed as fluorinating agents. The most important chlorite is $NaClO_2$ which is used to bleach textiles and paper pulp.

Compounds of chlorine(V). The best known chlorine(V) compounds are pentafluoride ClF_5, oxytrifluoride $ClOF_3$, dioxyfluoride ClO_2F, and derivatives of the trioxychlorate(V) $[ClO_3]^-$, trioxyfluorochlorate(V) $[ClO_3F]^{2-}$ and oxytetrafluorochlorate(V) $[ClOF_4]^-$ complexes:

ClF_5	$ClOF_3$	ClO_2F	(Cl_2O_5)
$[ClF_6]^-$	$[ClOF_4]^-$	$[ClO_3F]^{2-}$	$[ClO_3]^-$

The ClF_5 molecule has the shape of a tetragonal pyramid (see Fig. 51 and p. 276). Chlorine pentafluoride is an unstable gas (f.p. —93 °C, b.p. —13 °C). It is obtained by fluorinating ClF_3 (at 350 °C and 25 MPa):

$$ClF_3 + F_2 = ClF_5, \quad \Delta H^\circ_{298} = -33 \text{ kJ}$$

Methods of preparing derivatives of the $[ClF_6]^-$ complex are being sought for.

Chlorine dioxyfluoride ClO_2F (*chloryl fluoride*) is a quite stable colourless gas (f.p. —115 °C, b.p. —6 °C), obtained by fluorinating ClO_2. It is an acidic compound, which is hydrolysed as follows:

$$ClO_2F + H_2O = HClO_3 + HF$$

Derivatives of the $[ClO_3F]^{2-}$ complex are obtained by heating a solution of fluoride and chlorate for a long time:

$$CuF_2 + Cu[ClO_3]_2 = 2Cu[ClO_3F]$$

The $[ClO_3F]^{2-}$ complex is quite stable and only decomposes after prolonged boiling of its solutions.

A chlorine(V) oxide is not known. Derivatives of $[ClO_3]^-$ are called *chlorates*. The most important one is $KClO_3$ (*Berthollet's salt*), which is prepared by passing chlorine into a hot KOH solution

$$6OH^- + 3Cl_2 = 5Cl^- + ClO_3^- + 3H_2O$$

$$6KOH + 3\overset{0}{Cl_2} = 5K\overset{-1}{Cl} + K\overset{+5}{Cl}O_3 + 3H_2O$$

or by electrolysis of a hot KCl solution. $KClO_3$ is barely soluble in water and so is easily separated from KCl by cooling the solution.

Hydrogen trioxychlorate(V) $HClO_3$ has not been prepared in the free state, but (in contrast to HClO and $HClO_2$) concentrated solutions (to 40 per cent) are known. In an aqueous solution $HClO_3$ is strong *chloric* acid. It is prepared by an exchange reaction

$$Ba(ClO_3)_2 \text{ (sol)} + H_2SO_4 \text{ (sol)} = BaSO_4 \text{ (c)} + 2HClO_3 \text{ (sol)}$$

In its properties chloric acid resembles HNO_3. Mixed with hydrochloric acid it is a strong oxidant (of the aqua regia type).

When heated, chlorates undergo disproportionation:

$$4\overset{+5}{K}ClO_3 = 3K\overset{+7}{Cl}O_4 + K\overset{-1}{Cl}$$

and, in the presence of a catalyst, they decompose to liberate oxygen

$$2\overset{+5}{K}ClO_3 = 2K\overset{-1}{Cl} + 3\overset{0}{O_2}$$

When heated, trioxychlorates(V) are strong oxidants. In a mixture with reductants they are explosive. $KClO_3$ is used in the manufacture of matches and fireworks. Sodium chlorate, $NaClO_3$, is used as a weed-killer.

Compounds of chlorine(VII). The highest oxidation state of chlorine +7 is displayed in its oxide, some oxyfluorides, and the

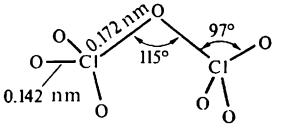
corresponding anion complexes:

Cl_2O_7	ClO_3F	ClO_2F_3	$ClOF_5$	(ClF_7)
$[ClO_4]^-$	$[ClO_3F_2]^-$	$[ClO_2F_4]^-$	—	—

Chlorine(VII) oxide Cl_2O_7 is a colourless liquid freezing at —93.4 °C and boiling at +83 °C. It is prepared by heating a mixture of hydrogen oxychlorate(VII) and phosphorus(V) oxide:

$$6HClO_4 + P_2O_5 = 3Cl_2O_7 + 2H_3PO_4$$

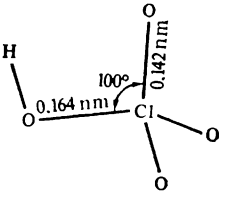
The Cl_2O_7 molecule is polar ($\mu = 0.24 \times 10^{-29}$ C·m). According to electronographic study it consists of two tetrahedra joined through an oxygen atom:



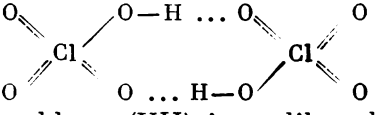
The oxide Cl_2O_7 is relatively stable but explodes when heated (above 120 °C).

The structure of the tetraoxychlorate(VII) ion ClO_4^- is tetrahedral, which, according to valence bond theory, corresponds to sp^3 hybridisation of the valence orbitals of chlorine atom stabilised by π bonding.

Tetraoxychlorates(VII) (still misnamed *perchlorates*) are very numerous. Most are readily soluble in water. Hydrogen tetraoxychlorate(VII) $HClO_4$ is a colourless liquid (f.p. —102 °C), capable of exploding. The structure of its molecule is



In the liquid state the molecules are dimerised through the hydrogen bond:



Hydrogen tetraoxychlorate(VII) is readily soluble in water, the solution being *perchloric acid*:

$$H_2O \cdots HClO_4 \rightleftharpoons OH_3^+ + ClO_4^-$$

Because of ionisation solutions of $HClO_4$ are quite stable. Perchloric acid is one of the strongest acids known. It is prepared by the action of concentrated sulphuric acid on $KClO_4$:

$$KClO_4 + H_2SO_4 = HClO_4 + KHSO_4$$

Numerous oxychlorates(VII) are known. The crystal hydrate $HClO_4 \cdot H_2O$, for example, is a perchlorate of oxonium $[OH_3]ClO_4$ (m.p. 49.9 °C). The most important of all oxychlorates(VII) is $KClO_4$, which is prepared by electrolysis of a solution of $KClO_3$. Perchlorates are mainly used in the manufacture of explosives and rocket propellants.

The molecule of ClO_3F has the form of a distorted tetrahedron ($\mu = 0.006 \times 10^{-29}$ C·m). In ordinary conditions chlorine trioxyfluoride (*perchloryl fluoride*) is a colourless gas (f.p. —147.8 °C and b.p. —46.7 °C). In contrast to Cl_2O_7 it has high thermal and hydrolytic stability, withstanding temperatures below 500 °C and not hydrolysing even at 260 °C. The acidic nature of ClO_3F is displayed during its interaction with concentrated solutions of alkali:

$$ClO_3F + 2NaOH = NaClO_4 + NaF + H_2O$$

ClO_3F, like Cl_2O_7, is a strong oxidant.

The other chlorine(VII) oxyfluorides (ClO_2F_3 and $ClOF_5$) are unstable gases, obtained by oxidising lower chlorine fluorides with oxygen fluorides:

$$ClF + O_2F_2 = ClO_2F_3; \quad ClF_3 + OF_2 = ClOF_5$$

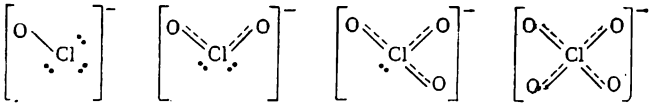
The +7 oxidation state of chlorine is displayed in certain cation complexes of the $ClO_2F_2^+$, ($ClOF_4^+$), and ClF_6^+ type. Derivatives of them $[ClF_6]^+[PtF_6]^-$, $[ClO_2F_2]^+[PtF_6]^-$ are formed by interaction with the very strong oxidant PtF_6 and certain compounds in which chlorine is in a lower oxidation state, e.g. ClO_2F, $ClOF_3$. The present position in the field of synthesis of fluoride and oxyfluoride derivatives of chlorine(VII) can be illustrated as follows (compounds that have not been obtained are shown in brackets):

Cations	*Molecules*	*Anions*
ClF_6^+	(ClF_7)	(ClF_8^-)
($ClOF_4^+$)	$ClOF_5$	($ClOF_6^-$)
$ClO_2F_2^+$	ClO_2F_3	$ClO_2F_4^-$
(ClO_3^+)	ClO_3F	$ClO_3F_2^-$

Cation complexes of chlorine with other oxidation states are also known, viz., ClF_2^+, ClF_4^+, $ClOF_2^+$, ClO_2^+. Like cations with N—F, N—O and O—F bonds, cation complexes of chlorine have a low bond energy and are therefore of great interest as components of compounds with high bond energies, ClF_5, F_2, OF_2, Cl_2O_7 are also such substances.

As the oxidation state rises in the series $ClO^- — ClO_2^- — ClO_3^- — ClO_4^-$, so does the stability of the anion complexes, which is due to the increasing number of electrons involved in the formation of bonds during the transition from ClO^- to ClO_4^-. The ClO_4^- ion in which all the valence electrons of the chlorine atom are involved in bond

formation is especially stable



The tetrahedral ClO_3F molecule and $[ClO_3F]^{2-}$ ion are very stable for the same reason.

In the series ClO^-—ClO_2^-—ClO_3^-—ClO_4^-, it is suggested, the role of π bonding increases. If the multiplicity of the bond in the ClO^- ion is unity, for example, then it is 1.5 in the ClO_4^- ion. The increasing multiplicity of the ClO bond corresponds to an increase in the mean energy of the bond, reduces the internuclear distance, and raises the force constant k. Thus d_{ClO} is 0.170 nm in ClO^- and 1.145 nm in ClO_4^-, while the force constants are 3.9 and 8.2 respectively. The characteristics of the ClO bonds in these ions are given in Table 32.

Table 32. **Characteristics of ClO bonds in $[ClO_n]^-$ anion complexes**

Anion complex	Bond characteristics		
	bond length, nm	bond energy, kJ/mol	bond angle ∠OClO
ClO^-	0.170	209	—
ClO_2^-	0.164	244.5	111°
ClO_3^-	0.157	243.7	106°
ClO_4^-	0.145	363.5	109°28′

Because of the increasing stability in the series ClO^-—ClO_2^-—ClO_3^-—ClO_4^-, oxidising activity decreases. Hypochlorites thus enter into redox reactions in any medium. Chlorates in solution oxidise only in an acid medium:

$$ClO_3^- + I^- + H_2O \rightarrow \text{practically no reaction}$$

$$ClO_3^- + 6I^- + 6H^+ = Cl^- + 3I_2 + 3H_2O$$

The ClO_4^- ion displays hardly any oxidising activity in solution.

The anions can also be deformed (excited) if heated sufficiently. Trioxychlorates(V) therefore behave like strong oxidants in melts, even in an alkaline medium:

$$\overset{+5}{K}\overset{+5}{Cl}O_3 + 3\overset{+4}{Mn}O_2 + 6NaOH \xrightarrow[\text{Fusion}]{} \overset{-1}{K}Cl + 3Na_2\overset{+6}{Mn}O_4 + 3H_2O$$

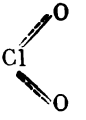
In the series $HClO—HClO_2—HClO_3—HClO_4$ the strength of the acids increases with the oxidation state of chlorine (see Table 21):

	HClO	$HClO_2$	$HClO_3$	$HClO_4$
pK_a	7.5	1.97	~—1	~—10

which is due to the strength of the O—H bond with a definite oxygen atom weakening as the number of oxygen atoms in the series $ClO^-—ClO_2^-—ClO_3^-—ClO_4^-$ increases.

Compounds of chlorine(II), (IV) and (VI). It can be taken that +2, +4, and +6 oxidation states of chlorine are displayed in the following oxides: Cl_2O_4, ClO_2, ClO_3, Cl_2O_6.

In ordinary conditions chlorine *dioxide* ClO_2 is a greenish yellow gas (f.p. —59 °C, b.p. 9.9 °C) with a pungent odour. It is an endothermic compound ($\Delta H_f^\circ = +105$ kJ/mol). Its molecule is angular ($\angle OClO = 118°$, $d_{ClO} = 0.148$ nm) so that it is polar ($\mu = 0.56 \times 10^{-29}$ C·m):



The molecule is paramagnetic since it has an odd number of elements.*

Thus ClO_2 is a valence-unsaturated compound that tends to take up or lose one electron

$$\overset{+4}{ClO_2} + e^- = \overset{+3}{ClO_2^-}, \quad \overset{+4}{ClO_2} - e^- = \overset{+5}{ClO_2^+}$$

The first tendency is the more marked (the electron affinity of ClO_2 being 3.43 eV), so that ClO_2 is a strong oxidant, oxidising PbO, for example, in an alkaline medium:

$$PbO + 2\overset{+4}{ClO_2} + 2NaOH = PbO_2 + 2\overset{+3}{NaClO_2} + H_2O$$

This reaction is used to obtain $NaClO_2$.

The loss of an electron from ClO_2 (ionisation potential 11.1 eV) is observed in salt-like compounds of the $[ClO_2]^+$ ion, e.g. $(ClO_2)[BF_4]$, $(ClO_2)_2[SiF_6]$, etc.

The tendency to gain or lose electrons is most easily realised during the disproportionation of ClO_2 in aqueous solutions (especially in alkaline solutions):

$$2\overset{+4}{ClO_2} + 2OH^- = \overset{+3}{ClO_2^-} + \overset{+5}{ClO_3^-} + H_2O$$

Two acids (or two salts) are formed as a result.

Chlorine dioxide decomposes gradually under light. It explodes when slightly heated, struck or brought into contact with combustible substances.

One of the industrial methods of obtaining ClO_2 is based on the reduction of $NaClO_3$ by heating with sulphur dioxide in a solution of sulphuric acid:

$$2NaClO_3 + SO_2 + H_2SO_4 = 2NaHSO_4 + 2ClO_2$$

Chlorine dioxide is used to bleach paper pulp, and as a strong oxidant in certain industrial processes.

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* For the structure of the ClO_2 and NO_2 molecules see Fig. 158.

The oxide Cl_2O_4 has only recently been obtained (1970). It has the structure of chlorine(I) chlorate(VII), $Cl—O—ClO_3$. It is a pale yellow liquid (b.p. 44.5 °C).

Chlorine trioxide ClO_3 is an unstable, short-lived radical discovered by the EPR method.

In ordinary conditions the oxide Cl_2O_6 is a dark red oily liquid, freezing at +3 °C. Its molecule is thought to have an unsymmetrical structure $O_2\overset{+5}{Cl}—O—\overset{+7}{Cl}O_3$. In the crystalline state it has an ionic structure (consisting of ClO_2^+ and ClO_4^- ions). The oxide is obtained by oxidising ClO_2 by ozone. It decomposes at ordinary temperatures and reacts energetically with water to form chloric and perchloric acids (through disproportionation):

$$Cl_2O_6\ (\overset{+5}{Cl}O_2—\overset{+7}{Cl}O_4^-) + HOH = \overset{+5}{H}ClO_3 + \overset{+7}{H}ClO_4$$

Cl_2O_6 explodes in contact with organic substances.

3.3. Bromine Subgroup

Bromine (Br), iodine (I) and astatine (At), having one unpaired electron (s^2p^5), have much in common with the typical elements of the group, but at high oxidation states they differ substantially from the typical elements.

The oxidation states of this subgroup are −1, +1, +3, +5, and +7. The −1 and +5 oxidation states are the most stable.

Bromine and its analogues are nonmetallic elements. Their nonmetallic character diminishes in the series Br—I—At with a rising number of electron shells. This is shown in particular by decreasing ionisation potential and electron affinity. Iodine and astatine also display marked amphoteric properties.

Bromine and iodine are quite abundant on Earth (see p 236). Natural bromine consists of two stable isotopes, ^{79}Br (50.56 per cent) and ^{81}Br (49.44 per cent). Iodine has one natural isotope, ^{127}I, but artificial isotopes have been produced.

Astatine is hardly encountered in nature but is obtained artificially, by bombarding bismuth, for example, with helium nuclei

$$^{209}_{83}Bi(\alpha,\ 2n)^{211}_{85}At$$

About 20 radioactive At isotopes have been synthesised, all with a very short half-life, the longest-lived being ^{211}At (half-life 8.3 hours). Astatine therefore cannot be obtained in appreciable quantities and its properties have not been adequately studied.

Bromine usually occurs in potassium minerals of chlorine. Bromine and iodine occur in sea water and oil-well brine, which are their main sources. Minute quantities of astatine are detected in products of the natural radioactive decay of uranium and thorium.

The simple substances. Certain characteristics of the simple substances of elements of the bromine subgroup and of the typical ele-

ments and also hydrogen are given below (for ordinary conditions):

	H	F	Cl	Br	I	At
State of aggregation	gas	gas	gas	liquid	solid	solid
Colour	colour-less	pale green	yellowish green	red-brown	black-violet	
M. p., °C	−259	−220	−101	−7	113	411
B. p., °C	−253	−188	−34	59	184	299
d_{EE}, nm	0.074	0.142	0.200	0.229	0.267	—
k_{EE}, N/m	573	719	327	245	172	—
$\Delta H_{diss.\ E_2}$, kJ/mol	435	159	243	199	150.7	117
$K_{diss.\ E_2}$	5.1×10^{-10}	9.2×10^{-3}	1.6×10^{-7}	3.3×10^{-5}	3.0×10^{-3}	—
E°_{298} $E_2 + 2e^- \rightleftarrows 2E^-$, V	−2.25	2.87	1.36	1.07	0.54	—

The molecules of bromine and its analogues are diatomic. As will be seen from the table above, the energy of dissociation of molecules $\Delta H_{diss.E_2}$ decreases with increasing intermolecular distance in the Br_2—I_2—At_2 series, which is due to the lower degree of overlapping of the bonding electron clouds. For the same reason the polarisability and intermolecular interaction of molecules increases, which accounts for the rise in the simple substances' melting and boiling points. In normal conditions bromine is a reddish brown liquid, iodine a blackish violet crystalline substance with a metallic lustre, and astatine a solid with a metallic appearance.

The solubility of halogens in water is relatively low. When their aqueous solutions are cooled, they precipitate crystal hydrates of a clathrate type ($E_2 \cdot 8H_2O$). The halogens are more soluble in organic solvents (alcohol, benzene, ether, carbon disulphide, etc.), a property that is utilised for extracting Br_2 and I_2 from various mixtures.

Bromine and iodine are quite strong oxidants, being inferior only to fluorine and chlorine. The oxidising activity of the simple substances decreases in the series F—At. Thus, the Gibbs' free energy of their reaction with hydrogen

$$1/2H_2 + 1/2Hal_2 = HHal$$

changes as follows:

	HF	HCl	HBr	HI
$\Delta G^{\circ}_{f,\ 298}$, kJ/mol	−273	−95	−53	1.8

Fluorine reacts explosively with hydrogen even in the cold. HBr is formed from the simple substances only when sufficiently heated, and HI only when strongly heated, the temperature being so high that a considerable part of it is decomposed thermally. Comparison of standard potentials of the halogens indicates that the oxidising activity of their molecules decreases with increasing atomic number of the element.

The oxidability (i.e. the reducing activity), on the contrary, increases markedly in the $Br_2—I_2—At_2$ series. Iodine, for example, is oxidised by concentrated nitric acid:

$$\overset{0}{3I_2} + 10\overset{+5}{H}\overset{+5}{N}O_3 = 6\overset{+5}{H}IO_3 + 10\overset{+2}{N}O + 2H_2O$$

The weakening of oxidising activity is also linked with the decreasing tendency of bromine and iodine to disproportionation reactions. Thus the hydrolysis constant

$$\overset{0}{E_2} + HOH \rightleftharpoons \overset{-1}{H}E + \overset{+1}{H}EO$$

decreases markedly in the series $Cl_2—Br_2—I_2$: 3×10^{-4}, 4×10^{-9} and 5×10^{-23}. In the transition from chlorine to iodine, consequently, the equilibrium of the reaction of halogens with water is shifted to the left.

The oxidising activity of bromine and iodine is widely employed in various syntheses and in chemical analysis. Iodine has been widely used as an antiseptic and haemostatic.

Bromine and iodine are obtained by oxidising bromides and iodides, for example

$$2\overset{-1}{NaE} + \overset{+4}{M}nO_2 + 2H_2SO_4 =$$
$$= \overset{0}{E_2} + \overset{+2}{M}nSO_4 + Na_2SO_4 + 2H_2O$$

Chlorine is often used as an oxidant to obtain bromine

$$2\overset{-1}{K}\overset{0}{Br} + \overset{0}{Cl_2} = 2\overset{-1}{K}Cl + \overset{0}{Br_2}$$

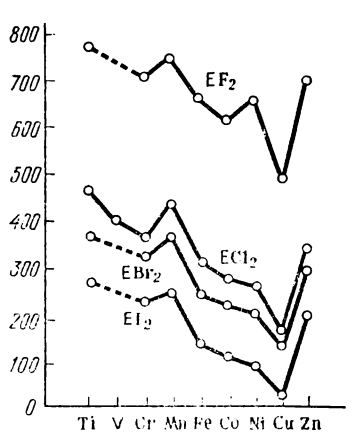


Fig. 144. Gibbs' energy of the formation of dihalides of 3*d* elements

Compounds of bromine (o.s. —1), iodine (o.s. —1), and astatine (o.s. —1). Bromine, iodine, and astatine react with less electronegative elements to form *bromides*, *iodides*, and *astatides*. In the series fluoride—chloride—bromide—iodide—astatide, the E—Hal bond weakens, and the stability of the compounds accordingly decreases. This is indicated in particular by comparison of the standard enthalpies and Gibbs' energies of the formation of halides of one and the same element (Fig. 144).

Bromides and iodides, unlike fluorides, are mainly known for elements with low oxidation states. Fluorides and chlorides are known, for example, for uranium in all oxidation states (UCl_3,

UCl_4, UCl_5, UCl_6) but bromides and iodides are known only for U(III) and U(IV) (UBr_3 and UBr_4; UI_3 and UI_4).

Bromides and iodides (like fluorides and chlorides) can be ionic, ionic-covalent, or covalent compounds. Bromides and iodides of the alkali and alkaline earth metals are predominantly ionic, while those of nonmetals are mainly covalent. The covalent character of the bond increases in the halide series of one and the same element with its increasing oxidation state.

Most bromides and iodides are readily soluble in water, the exceptions being (as with chlorides) AgE, AuE, CuE, PbE_2, and certain others. The solubility of ionic halides in water changes as follows: iodide > bromide > chloride > fluoride. The decreasing solubility in this series is due to the solubility depending on the lattice energy, which increases with the decreasing ionic radius of halogens. This rule holds for halides of the alkali and alkaline earth metals and lanthanides. Fluorides of the last two are practically insoluble. For crystalline halides, in which a covalent bond is clearly manifested, the solubility of the fluoride can be high and that of iodide low, as, for example, with Ag(I) and Hg(II).

Bromides and iodides, like hydrides, fluorides, and chlorides may be basic (halides of the alkali and alkaline earth metals) or acidic (halides of nonmetals), depending on the properties of the element in its positive oxidation state. Examples of bromides and iodides of various chemical nature, and their behaviour during hydrolysis, are given below:

$$KBr + HOH \rightleftharpoons \text{practically no reaction}$$

$$\underset{\text{Basic}}{NaI} + HOH \rightleftharpoons \text{practically no reaction}$$

$$BBr_3 + 3HOH = H_3BO_3 + 3HBr$$

$$\underset{\text{Acidic}}{PI_3} + 3HOH = H_3PO_3 + 3HI$$

The difference in the chemical nature of bromides and iodides can also be seen in the following reactions

$$KBr + AlBr_3 = K[AlBr_4]$$

$$\underset{\text{Basic}}{2KI} + \underset{\text{Acidic}}{HgI_2} = K_2[HgI_4]$$

Such reactions are less frequent between bromides or iodides than between the corresponding fluorides or chlorides; the coordination numbers of the complexing agents are also not usually the highest ones.

Selected constants of hydrogen halogenates are given below:

	HF	HCl	HBr	HI
ΔH_f°, kJ/mol	−270.9	−92.8	−34.1	+26.6
ΔG_f°, kJ/mol	−272.8	−94.79	−53.2	+1.8
d_{HHal}, nm	0.092	0.128	0.141	0.160

	HF	HCl	HBr	HI
k_{HHal}, N/m	966	516	412	314
E_{HHal}, kJ/mol	565	431	364	297
$\mu \times 10^{29}$, C·m	0.640	0.347	0.263	0.127
M. p., °C	−83	−114	−88	−51
B. p., °C	19	−85	−67	−36
K_a	6.6×10^{-4}	1×10^{7}	1×10^{9}	1.6×10^{11}

Table 33. **Data for Calculating the ΔG°_{298} of the Ionisation of Hydrohalic Acids in Aqueous Solution**

Process	ΔG°_{298}, kJ/mol			
	HF	HCl	HBr	HI
HHal (sol) = HHal (g)	24	−4	−4	−4
HHal (g) = H (g) + Hal (g)	537	405	340	269
H (g) = H^+ (g) + e^-	1324	1324	1324	1324
Hal (g) + e^- = Hal^- (g)	−349	−368	−344	−316
H^+ (g) + Hal^- (g) = H^+ (sol) + Hal^- (sol)	−1518	−1398	−1368	−1334
HHal (sol) = H^+ (sol) + Hal^- (sol)	18	−41	−52	−61

The molecules of HHal are polar. In the series HF—HCl—HBr—HI, the dipole moment decreases while polarisability of the molecules increases. For that reason, the melting and boiling points in the series HCl—HBr—HI increase (see Fig. 142). In ordinary conditions the bromide and iodide of hydrogen are gases readily soluble in water. As will be seen from Table 33, their solutions are strong acids (*hydrobromic* and *hydriodic* acids respectively). Acid strength increases in the series HF—HCl—HBr—HI, which is mainly determined by the decreasing strength of the H—Hal bond in this series. This bond is especially strong in HF, so that hydrofluoric acid the weakest of all the hydrohalic acids.

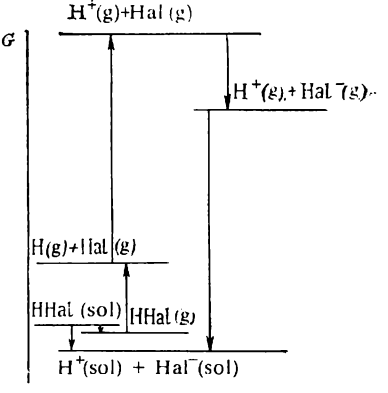


Fig. 145. Diagram for calculating the Gibbs' energy of the reaction HHal (sol) = H^+ (sol) + Hal (sol) (Hal = Cl, Br, I)

Figure 145 and Table 33 can be used to calculate the enthalpies and Gibbs' energies of ionisation of hydrohalic acids. The diagram includes the following processes: (1) the dehydration of the HHal molecule; (2) the dissociation of HHal molecules into atoms; (3) the conversion of the H and Hal atoms into H^+ and Hal^- ions respectively; (4) the hydration of the H^+ and Hal^- ions.

As will be seen from Table 33, the process

$$HHal\ (sol) \rightleftarrows H^+\ (sol) + Hal^-\ (sol)$$

is characterised in accordance with $\Delta G^\circ = -RT \ln K$ by the following values of pK_a

	HF	HCl	HBr	HI
pK_a	3.1	−7.1	−9.1	−10.7

The tabulated data show that the ΔG° of decomposition of the HHal molecules into atoms mainly determines the difference in the values of ΔG_a° and hence pK_a.

As the internuclear distance increases and bond energy diminishes, the stability of the molecules in the series HF—HCl—HBr—HI decreases along with increasing reducing activity. For example, for the reaction

$$2\overset{-1}{H}Hal\ (g) + \overset{+6}{H_2}SO_4\ (l) = \overset{0}{Hal_2}\ (g) + \overset{+4}{SO_2}\ (g) + 2H_2O\ (l)$$

the Gibbs' energy changes as follows:

	HF	HCl	HBr	HI
ΔG°_{298}, kJ/mol	460	105	25	−68

It therefore follows that HF and HCl do not react with H_2SO_4, while HI undergoes an oxidation-reduction reaction. The hydrogen halides also do not react with concentrated sulphuric acid: HF and HCl do not react at all, while HBr reduces concentrated H_2SO_4 to SO_2 (when heated) and HI to H_2S:

$$8\overset{-1}{H}I\ (g) + \overset{+6}{H_2}SO_4\ (l) = 4\overset{0}{I_2}\ (c) + \overset{-2}{H_2}S\ (g) + 4H_2O\ (l)$$

$$\Delta G^\circ_{298} = -287\ kJ$$

HBr and HI therefore cannot be prepared by reacting sulphuric acid and their salts. Unlike fluoride and chloride, they are usually obtained by hydrolysis of phosphorus bromide and phosphorus iodide.

Compounds of bromine(I), iodine(I), and astatine(I). The + 1 oxidation state of bromine and its analogues is observed in compounds with more electronegative halogens and oxygen, e.g.:

BrF	BrCl	Br_2O	IF	ICl	IBr	—
BrF_2^-	$BrCl_2^-$	BrO^-	IF_2^-	ICl_2^-	IBr_2^-	IO^-

Bromine (I) Compounds

BrF red gas, f.p.—33 °C, b.p. 20 °C
BrCl yellow gas, f.p.—54 °C, b.p. 5 °C (decomposes)
Br_2O reddish brown solid, f. p.—17 °C

Iodine (I) Compounds

IF only discovered spectroscopically
ICl red solid, m.p. 27 °C b.p. 97 °C (decomposes)
IBr grey solid, m. p. 42 °C, b. p. 119 °C (decomposes)

Binary compounds of bromine(I) and iodine(I), except Br_2O, are formed by direct interaction of the simple substances. The compounds, except ICl, are very unstable ($\Delta H^\circ_{298} = -12$ kJ/mol).

The binary compounds of bromine(I) and iodine(I) are acidic in chemical nature as is shown, in particular, by their reaction with water:

$$Br_2O + HOH = 2HBrO, \qquad ICl + HOH = HIO + HCl$$

Their acidic nature is also revealed during their interaction with similar derivatives of the alkali and alkaline earth metals:

$$KCl + ICl = \underset{\text{Dichloroiodate (I)}}{K[ICl_2]}, \qquad CsI + AtI = \underset{\text{Diiodoastate (I)}}{Cs[AtI_2]}$$

Iodides of the alkali metals are very liable to join halogen molecules in solution to form *polyhalides*. The interaction of a basic iodide of an alkali metal and an acidic iodide of iodine(I), $\overset{+1}{I}\,I$ can be regarded as such a reaction:

$$\overset{-1}{K}\overset{+1}{I}\overset{-1}{I} = \underset{\text{Diiodoiodate (I)}}{K[\overset{+1}{I}\overset{-1}{I}_2]}, \qquad I^-(aq) + I_2(aq) = I_3^-(aq)$$

The ions $[ICl_2]^-$, $[IBr_2]^-$, $[II_2]^-$, $[BrBr_2]^-$, $[BrCl_2]^-$ have a linear structure. The central atoms of the complexes are positively charged, while the peripheral ones have negative effective charges. In the $[ICl_2]^-$ ion, for example, $\delta_I = 0.11+$, $\delta_{Cl} = 0.55-$; in the $[II_2]^-$ ion the effective charge of the peripheral atoms of iodine is 0.5—. Compounds containing complexes of the type $[I(BrCl)]^-$ and $[Br(BrCl)]^-$ are also known.

According to the MO theory, the structure of these ions is due to the formation of molecular orbitals through the combination of three atomic p_x orbitals (see Fig. 139).

In addition to binary compounds, unstable covalent compounds of the type $BrNO_3$, INO_3, $IClO_3$ are also known for bromine(I) and iodine(I). These are yellow substances formed by disproportionation of iodine and bromine in nonaqueous (e.g. ether) solutions in the presence of silver salts:

$$I_2 + AgNO_3 = AgI + INO_3$$

The hydrolysis of nitrates, chlorates, and like compounds of bromine(I) and iodine(I), is evidence of their acidic character: for example,

$$IClO_4 + HOH = HIO + HClO_4$$

Their relation to basic compounds is further evidence:

$$KNO_3 + INO_3 = K[I(NO_3)_2]$$

Derivatives of EO^- (*hypobromites* and *hypoiodites*) are similar in their properties and methods of preparation to hypochlorites. When heated they easily undergo disproportionation:

$$3\overset{+1}{K}E\overset{-1}{O} = 2KE + K\overset{+5}{E}O_3$$

or decompose to liberate oxygen:

$$\overset{+1}{2KE}\overset{-1}{O} = 2K\overset{-1}{E} + \overset{0}{O_2}$$

Hydrogen oxybromate(I) HBrO and hydrogen oxyiodate(I) HIO are known only in dilute aqueous solutions, which are weak acids (like HClO) known as *hypobromous* and *hypoiodous* acid. Like HClO, they decompose easily when heated, and on exposure to light:

$$HEO\ (sol) = HE\ (sol) + 1/2\ O_2\ (g)$$

The change in ΔG°_{298} for HClO in this process is −51 kJ/mol, for HBrO −5, and for HIO +55 kJ/mol. This corresponds to the growth of relative stability in the series HClO—HBrO—HIO.

The derivatives of bromine(I) and iodine(I) are strong oxidants.

Compounds of bromine(III) and iodine(III). Bromine and iodine have an oxidation state of +3 in their trihalides and corresponding anion complexes:

BrF_3	IF_3	ICl_3
$[BrF_4]^-$	$[IF_4]^-$ (?)	$[ICl_4]^-$

Oxides of E(III) are not known; their corresponding anions EO_2^- and IO_2^- are unstable and liable to disproportionation.

Stable yellow $I(ClO_4)_3$, $I(NO_3)_3$, $I(IO_3)_3$, etc., are known for iodine(III)

The structure of the trihalides is similar to that of ClF_3 (see Fig. 140), i.e. they have a T-shape configuration. The trihalides of bromine and iodine (except liquid BrF_3) are low-melting solids, they are acidic compounds with certain signs of amphoterity. Their hydrolysis is accompanied with disproportionation, e.g.:

$$BrF_3 + 2HOH = HBrO_2 + 3HF$$

$$3HBrO_2 = 2HBrO_3 + HBr$$

$$\overset{+3}{3}BrF_3 + 6HOH = \overset{+5}{2}HBrO_3 + 9HF + \overset{-1}{HBr}$$

Compounds of the $I(NO_3)_3$ type are hydrolysed in a similar way:

$$3I(NO_3)_3 + 6HOH = 2HIO_3 + 9HNO_3 + HI$$

The acidic character of the halides of Br(III) and I(III) is also confirmed by the existence of derivatives of the $[BrF_4]^-$ and $[ICl_4]^-$ complexes. The formation of potassium tetrachloroiodate(III), for example, can be represented by the following equation

$$KCl + ICl_3 = K[ICl_4]$$

Tetrahalohalate(III) complexes have a square con guration (see Fig. 51*g*). Four bonds lie along the axes of the square with two nonbonding electron pairs above and below the plane of bond distribution. According to the molecular orbital theory, the square structure of tetrahalohalate(III) complexes corresponds to two perpendicular three-centre Hal—E—Hal bonds.

The central atoms of the $[EHal_4]^-$ complexes are positively charged and the peripheral ones negatively. In the ion $[ICl_4]^-$ for example, $\delta_I = 1.07$ and $\delta_{Cl} = 0.52$.

In the liquid state the halides of Br(III) and I(III) are partly ionised: for example,

$$\underset{\text{Donor}}{BrF_3} + \underset{\text{Acceptor}}{BrF_3} \rightleftarrows BrF_2^+ + BrF_4^-$$

This type of ionisation is evidence of the amphoteric properties of the BrF_3 molecules, which can act as both donors and acceptors of F^- ions. Thus, BrF_3 (m.p. 7.9 °C, b.p. 126 °C) reacts with basic fluorides to form fluorobromates(III):

$$\underset{\text{Acceptor}}{KF} + BrF_3 = K[BrF_4]$$

and with more acidic fluorides to form derivatives of the cationic difluorobromyl(III) complex BrF_2^+:

$$\underset{\text{Donor}}{BrF_3} + SbF_5 = [BrF_2][SbF_6]$$

This property of trihalides explains their use as nonaqueous solvents for the corresponding syntheses. Bromine trifluoride is used as a fluorinating agent.

Derivatives of the cationic *oxyiodyl*(III) complex IO^+ are also known, for example, $(IO)_2SO_4$ and $(IO)NO_3$, which are salt-like yellow crystals.

Derivatives of bromine(III) and iodine(III) are strong oxidants.

Compounds of bromine(V) and iodine(V). Bromine and iodine have a +5 oxidation state in the following compounds and their corresponding complexes:

BrF_5	BrO_2F	—
$[BrF_6]^-$	—	$[BrO_3]^-$
IF_5	IO_2F	I_2O_5
$[IF_6]^-$	$[IO_2F_2]^-$	$[IO_3]^-$

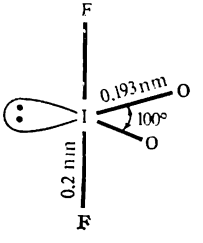
The fluorides, oxides, and oxyfluorides of bromine(V) and iodine(V) are colourless. BrI_5 (f.p. −62 °C). IF_5 (m.p. 9.6 °C), and BrO_2F (f.p. −9 °C) are liquids, and I_2O_5 and IO_2F solids. Unlike bromine(V) derivatives, iodine(V) compounds are quite stable; I_2O_5 and IO_2F, for example, begin to decompose only at temperatures above 300 °C. All react more or less energetically with water to form acids

$$I_2O_5 + H_2O = 2HIO_3$$
$$BrF_5 + 3H_2O = HBrO_3 + 5HF$$
$$IO_2F + H_2O = HIO_3 + HF$$

and with basic compounds to give the corresponding salts, for example,

$$KF + IF_5 = K[IF_6]$$
$$6KOH + IF_5 = K[IO_3] + 5KF + 3H_2O$$

Derivatives of the $[IO_2F_2]^-$ complex



are formed through the interaction of trioxyiodates(V) and concentrated HF:

$$KIO_3 + 2HF = K[IO_2F_2] + H_2O$$

Derivatives of $[EO_3]^-$ are known as *bromates* and *iodates*. The $[EO_3]^-$ anions are quite stable, so that it is they which are usually formed in aqueous solutions when strong oxidants act on bromine, iodine, and astatine compounds:

$$\overset{0}{Br_2} + 5Cl_2 + 6H_2O = 2H\overset{+5}{Br}O_3 + 10HCl$$

$$\overset{0}{2At} + 5HClO + H_2O = 2H\overset{+5}{At}O_3 + 5HCl$$

The aqueous solutions of $HBrO_3$ and HIO_3 are acids known as *bromic* and *iodic* respectively. In the series $HClO_3$—$HBrO_3$—HIO_3 the acidic properties weaken, and stability, on the contrary, increases so that, while $HClO_3$ can exist only in solution, HIO_3 can be isolated in the free state. Solid hydrogen trioxyiodate(V) is a white crystalline solid (m.p. 110 °C), which can be isolated by the action of sulphuric acid on iodates. When HIO_3 is heated, I_2O_5 is produced.

The iodates of other elements are also much more stable than the corresponding chlorates and bromates. Some iodates occur in nature: KIO_3, for example, as an admixture in Chile nitre, and $NaIO_3$ as the independent mineral *lautarite*.

When strongly heated, bromates and iodates decompose, liberating oxygen.

Compounds of bromine(VII) and iodine(VII). The inner periodicity is markedly displayed in the series of compounds of Cl(VII)—Br(VII)—I(VII) (see p. 273). In contrast to Cl and I, an oxidation state of +7 is not characteristic of Br. Heptafluoride IF_7, trioxyfluoride IO_3F, and derivatives of tetraoxyiodate $[IO_4]^-$ and hexaoxyiodate $[IO_6]^{5-}$ anions are known for iodine with the highest oxidation state:

IF_7	IO_3F	—
—	—	IO_6^{5-}

Compounds of bromine(VII) have only recently been obtained. These are heptafluoride BrF_7 and derivatives of the BrO_4^- ion.

Heptafluorides EF_7 are very reactive gases, and are acidic compounds in nature, as can be clearly seen from their hydrolysis:

$$IF_7 + 6H_2O = H_5IO_6 + 7HI$$

Iodine trioxyfluoride IO_3F is a white crystalline substance decomposing at temperatures above 90 °C with partial liberation of oxygen.

The coordination number of six (with respect to oxygen) characteristic of elements of the fifth period is realised in the IO_6^{5-} ion.

so that it is stable. The IO_6^{5-} ion has an octahedral shape with the iodine atom at the centre ($d_{IO} = 0.185$ nm).

Hydrogen hexaoxyiodate(VII) H_5IO_6 (*periodic acid*)* is a colourless crystalline solid (m.p. 122 °C), soluble in water. Its acidic properties are much less marked ($K_{a1} = 3.1 \times 10^{-2}$, $K_{a3} = 2.5 \times \times 10^{-13}$) than those of $HClO_4$; when neutralised it usually produces acidic salts. Hexaoxyiodates(VII) (*periodates*) are obtained from iodates(V), or by a disproportionation reaction

$$5\overset{+5}{Ba}(\overset{+5}{I}O_3)_2 = \overset{+7}{Ba_5}(\overset{+7}{I}O_6)_2 + 4\overset{0}{I_2} + 9O_2$$

or by oxidation with chlorine in an alkaline medium

$$\overset{+5}{K}\overset{+5}{I}O_3 + Cl_2 + 6KOH = \overset{+7}{K_5}\overset{+7}{I}O_6 + 2KCl + 3H_2O$$

or electrolytically.

Hydrogen hexaoxyiodate(VII) is obtained by the action of sulphuric acid on barium hexaoxyiodate(VII)

$$Ba_5(IO_6)_2 + 5H_2SO_4 = 5BaSO_4\downarrow + 2H_5IO_6$$

Tetraoxybromates(VII) (*perbromates*) are formed by oxidising trioxybromates(V) in an alkaline medium: e.g., with fluorine:

$$\overset{+5}{Na}\overset{+5}{Br}O_3 + F_2 + 2NaOH = \overset{+7}{Na}\overset{+7}{Br}O_4 + 2NaF + H_2O$$

$HBrO_4$ has not been obtained in the free state and its aqueous solutions only have been obtained. *Perbromic* acid is close in strength to perchloric acid. Its oxidising power is greater than that of perchloric and periodic acid.

$$BrO_4^- + 2H^+ + 2e^- = BrO_3^- + H_2O, \quad E^\circ_{298} = 1.8 \text{ V}$$
$$ClO_4^- + 2H^+ + 2e^- = ClO_3^- + H_2O, \quad E^\circ_{298} = 1.19 \text{ V}$$

Bromine and iodine compounds are used mainly in medicine, in various syntheses, and in chemical analysis.

CHAPTER 4

Group VI p Elements

Group VI *p* elements comprise the typical elements oxygen O and sulphur S, and the elements of the selenium subgroup, viz., selenium Se, tellurium Te, and polonium Po:

O	$1s^22s^22p^4$
S	$2s^22p^63s^23p^4$
Se	$3s^23p^63d^{10}4s^24p^4$
Te	$4s^24p^64d^{10}5s^25p^4$
Po	$4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^4$

* The acid is the $EO(OH)_n$ type (see Table 21) while $HClO_4$ is an acid of the $EO_3(OH)_n$ type.

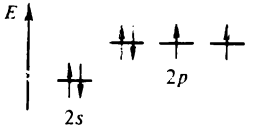
Selected characteristics of these elements are as follows.

	$_8$O	$_{16}$S	$_{34}$Se	$_{52}$Te	$_{84}$Po
Atomic mass	15.9994	32.064	78.96	127.60	[210]
Valence electrons	$2s^22p^4$	$3s^23p^4$	$4s^24p^4$	$5s^25p^4$	$6s^26p^4$
Covalent radius of atom, nm	0.066	0.104	0.114	0.132	—
Metallic radius of atom, nm	—	—	0.16	0.17	0.17
Conventional radius of E^{2-} ion, nm	0.136	0.182	0.193	0.211	—
Conventional radius of E^{6+} ion, nm	—	0.029	0.035	0.056	—
Ionisation energy $E^0 \rightarrow E^+$, eV	13.62	10.36	9.75	9.01	8.43
Electron affinity, eV	1.47	2.08	2.02	about 2	1.35
Abundance, mole per cent	58.0	0.03	1.5×10^{-5}	1.3×10^{-7}	2×10^{-15}

This table shows that ionisation energy decreases in the series O—S—Se—Te—Po together with an increase in the size of atoms and ions. This reduces the nonmetallic character of the elements so that, while oxygen is a nonmetal, polonium is a metal.

4.1. Oxygen

The electron configuration of the oxygen atom in the ground state is $1s^22s^22p^4$



Like fluorine, oxygen forms compounds with almost all elements, except helium, neon and argon. Since its electronegativity is inferior only to that of fluorine, its oxidation state in most compounds is —2. It can also, moreover, have oxidation states of +2 and +4, and +1 and —1 in its compounds with an O—O bond.

Oxygen is the most abundant element on the Earth (58.0 mole fractions). It consists of three stable isotopes: ^{16}O (99.759 per cent), ^{17}O (0.037 per cent) and ^{18}O (0.204 per cent). Isotopes ^{14}O, ^{15}O and ^{19}O have been obtained artificially; their half-life periods are measured by tens of seconds.

Because of its abundance and high oxidising activity, oxygen predetermines the form of existence of all other elements in the Earth. Its importance was particularly great during the formation of the crust. It is supposed that oxygen appeared in the atmosphere as a result of secondary processes, e.g. the vital processes of green plants.

The simple substance. The most stable form of oxygen is the diatomic molecule O_2. Magnetochemical research has shown that it is paramagnetic, the magnitude of its paramagnetism being in agreement with the presence of two unpaired electrons:

$$[\sigma_s]^2 [\sigma_s^*]^2 [\sigma_z]^2 [\pi_{x,\,y}]^4 [\pi_x^*]^1 [\pi_y^*]^1$$

The O_2 molecule has four antibonding electrons for eight bonding ones, its bond order therefore being 2. Bearing in mind the paramagnetism and bond order the structure of the O_2 molecule can be described as follows:

$$:O\overset{\cdot\cdot\cdot}{=}O: \quad \text{or} \quad :\dot{O}\equiv\dot{O}:^*$$

Because of its bond order, the interatomic distance in O_2 (0.1207 nm) is shorter than the length of a single bond O—O (0.148 nm). For that reason the O_2 molecule is very stable, its dissociation energy being 494 kJ/mol (k = 1140 N/m), while the energy of a single O—O bond is only 210 kJ/mol (k = 380 N/m). The dissociation of O_2 molecules into atoms only becomes noticeable at temperatures above 2000 °C. Dissociation also occurs during the absorption of ultra-violet radiation (photolysis).

The freezing (—218.9 °C) and boiling (—183 °C) points of oxygen are very low. It dissolves poorly in water (five volumes in 100 volumes at 0 °C). Liquid and solid oxygen are attracted by a magnet.

The allotropic form of oxygen, *ozone* O_3, can be regarded as a compound of O(IV).

Oxygen is very active chemically, especially at high temperatures and in the presence of catalysts. It reacts directly with most simple substances to form oxides of them; only with fluorine does it behave as a reducing agent.

Oxygen is obtained by rectifying liquid air, and as a by-product of the electrolysis of water. In the laboratory it is obtained by thermal decomposition of oxygen-rich compounds, e.g. $KMnO_4$, $KClO_3$, etc.

Compounds of oxygen (o.s. — 2). As already mentioned, it is not energy-wise for simple anions of E^{n-} with two or more charges to be formed (see p 45). Compounds containing O^{2-} ions therefore do not exist in nature. Even in the crystalline oxides of most active metals of the Na_2O and CaO type the effective charge of oxygen is only around 1—.

As in the other *p* elements of the second period, the maximum valence (the number of two-electron two-centre bonds) of oxygen is four. Its atoms can be in sp^3, sp^2, or sp hybridisation states corresponding to a tetrahedral, triangular,

* The three dots in the first formula represent the bond formed by two π bonding and one π^* antibonding electron which corresponds to a bond multiplicity of 0.5. In the second formula, the unpaired dots designate π^* electrons. When excited, O_2 molecule becomes diamagnetic, which corresponds to the formula $:\ddot{O}=\ddot{O}:$.

or linear arrangement of the σ bonds. Examples of compounds in which these hybrid states of the oxygen orbitals are displayed are respectively crystalline BeO (see Fig. 69*c*), TiO_2 (see Fig. 70*b*), and SiO_2 (see Fig. 70*c*).

There is also many oxides in which the coordination number of oxygen exceeds its maximum valence (i.e. is higher than four). In the crystal of MgO, for example, the coordination number of oxygen is six, and in the crystal of Na_2O eight. Molecular orbital theory explains this by each O atom in the MgO crystal (NaCl structural type) being linked by three hypervalent (three-centre) bonds (through $2p_x$, $2p_y$, and $2p_z$ orbitals with six neighbouring Mg atoms). Crystalline MnO, FeO, CoO, NiO, and other oxides with an NaCl type structure are built similarly.

In oxides of the Na_2O type (K_2O, Rb_2O, Li_2O) the oxygen atoms are linked (through their 2*s*, $2p_x$, $2p_y$ and $2p_z$ orbitals) with eight neighbouring metal atoms by means of four three-centre bonds.

The composition of crystalline oxides (in particular of *d* elements) is more or less variable; for MnO, for instance, it varies from MnO to $MnO_{1.5}$, and for Mn_2O_3 from $MnO_{1.5}$ to $MnO_{1.6}$. If the oxygen content of oxides is greater than the stoichiometric ratio, they display hole type conductivity; when the metal content is above the stoichiometric level, electron type conductivity is observed. MnO, Cu_2O, FeO, and other oxides are semiconductors with hole conductivity. Some oxides, whose composition does not obey the normal rules of oxidation states (e.g. Cr_3O, Ti_6O, Ti_3O) are metallic compounds.

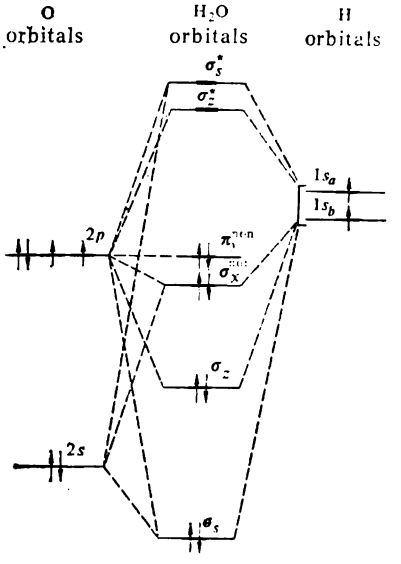


Fig. 146. Energy diagram of the orbitals of an H_2O molecule

The most important oxide is water (hydrogen oxide). Suffice it to say that it constitutes 50 to 99 per cent of the mass on any living organism. Human blood is over four-fifths water; the water content of the muscles is 35 per cent. With an average expectation of life (70 years), a person has to drink about 25 tonnes of water.

As already mentioned (Fig. 50) the water molecule has an angular configuration, which corresponds, according to the valence bond theory, to an sp^3 hybrid state of the oxygen atom; two sp^3 hybrid orbitals are involved in the formation of the two O—H bonds of the water molecule. Two nonbonding electron pairs are located in the other two sp^3 hybrid orbitals (see Fig. 50). The bond angle of the water molecule $\angle$HOH is 104.5°.

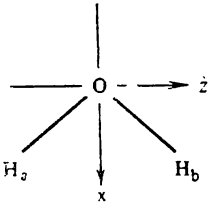
Within the context of molecular orbital theory, the model of the water molecule described corresponds to a distribution of eight valence electrons in two bonding and two nonbonding molecular

orbitals

$$[\sigma_s]^2\,[\sigma_z]^2\,[\sigma_x^{non}]^2\,[\pi_y^{non}]^2$$

and the presence of two unoccupied antibonding orbitals (see Fig. 146). This explanation is confirmed by the presence of four first ionisation potentials (27.3, 16.2, 14.5 and 12.6 eV) in the H_2O molecule.

From the standpoint of molecular orbital theory, the structure of the water molecule can be explained as follows. The oxygen and hydrogen atoms are arranged as shown in the diagram.



The molecular orbitals are formed by 2*s* and 2*p* orbitals of the oxygen atom and 1*s* orbitals of the two hydrogen atoms. The way these orbitals overlap is shown in Fig. 147.

The overlapping of the $2p_z$ orbitals of the oxygen atom and 1*s* orbitals of the two hydrogen atoms gives rise to molecular σ_z bonding and σ_z^* antibonding orbitals. As will be seen from Fig. 147, the 2*s* and $2p_x$ orbitals of oxygen overlap in a similar way. Three molecular orbitals are formed as a result: bonding σ_s, almost nonbonding σ_x^{non}, and antibonding $\sigma_{s(x)}^*$. The $2p_y$ orbital is perpendicular

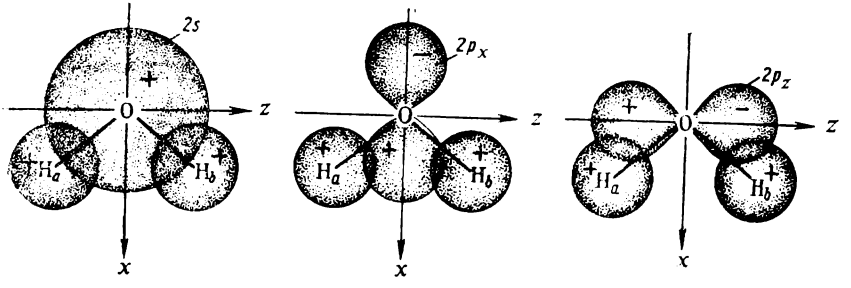


Fig. 147. Overlapping of the 2*s*, $2p_x$ and $2p_z$ orbitals of the oxygen atom with the 1*s* orbitals of the two hydrogen atoms in a molecule of water

to the plane of the H and O atoms; it does not overlap with the 1*s* orbitals of the hydrogen atoms, and acts as a nonbonding molecular π_y^{non} orbital in the water molecule.

The combination of the initial four atomic orbitals of the oxygen atom and two orbitals of the hydrogen atoms thus yields two bonding (σ_s and σ_z), two nonbonding (σ_x^{non} and π_y^{non}), and two antibonding (σ_s^* and σ_z^*) molecular orbitals (see Fig. 146).

In accordance with the nature of the element in its positive oxidation state, the character of the oxides changes regularly through the periods and groups of the periodic system. In the periods, the negative effective charge δ_0 of the oxygen atoms decreases, and the oxides' properties gradually change from basic through amphoteric to acidic:

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
Effective charge δ_0*	−0.81	−0.35	−0.31	−0.23	−0.13	−0.06	−0.01
Acid-base properties of the oxide	Basic		Amphoteric		Acidic		
	strong	weak		weak	medium		strong

The difference in properties of the various oxides is seen in their reaction with water

$$\underset{\text{Basic}}{Na_2O} + H_2O = 2NaOH, \qquad 3H_2O + \underset{\text{Acidic}}{P_2O_5} = 2H_3PO_4$$

and during their interaction with each other

$$\underset{\text{Basic}}{3CaO} + \underset{\text{Acidic}}{P_2O_5} = Ca_3(PO_4)_2$$

Amphoteric oxides do not react with water but can react with acids and alkalis:

$$\underset{\text{Basic}}{Al_2O_3}\ (c) + 6HCl\ (sol) + 9H_2O\ (l) = 2\,[Al(OH_2)_6]\,Cl_3\ (sol)$$

$$6NaOH\ (sol) + \underset{\text{Acidic}}{Al_2O_3}\ (s) + 3H_2O\ (l) = 2Na_3[Al(OH)_6]\ (sol)$$

and during fusion with acidic and basic oxides.

A comparative, quantitative assessment of the acid-base properties of oxides can be derived from ΔG of corresponding analogous reactions. The decreasing ΔG°_{298} in the reactions

$Na_2O\ (c) + H_2O\ (l) = 2NaOH\ (c)$, $\Delta G^\circ_{298} = -148$ kJ

$MgO\ (c) + H_2O\ (l) = Mg(OH)_2\ (c)$, $\Delta G^\circ_{298} = -27$ kJ

$1/3\ Al_2O_3\ (c) + H_2O\ (l) = 2/3\ Al(OH)_3\ (c)$, $\Delta G^\circ_{298} = +7$ kJ

indicates a weakening of basic properties and reactivity toward water in the series Na_2O—MgO—Al_2O_3. In the P_2O_5—SO_3—Cl_2O_7

$1/3\ P_2O_5\ (c) + H_2O\ (l) = 2/3\ H_3PO_4\ (c)$, $\Delta G^\circ_{298} = -59$ kJ

$SO_3\ (l) + H_2O\ (l) = H_2SO_4\ (l)$, $\Delta G^\circ_{298} = -70$ kJ

$Cl_2O_7\ (g) + H_2O\ (l) = 2HClO_4\ (l)$, $\Delta G^\circ_{298} = -329$ kJ

on the contrary, the negative value of ΔG°_{298} increases, which indicates strengthening of the acidic character of the oxides.

Peroxides. The electron affinity of the O_2 molecule is 0.8 eV and its ionisation energy 12.08 eV. During chemical transformations

* See footnote to p. 88.

it may accept or lose electrons to form molecular ions of the O_2^{2-}, O_2^-, and O_2^+ type (see Table 34).

Table 34. Bond Energy, Length and Order in the O_2 Molecule and Molecular Ions O_2^+, O_2^- and O_2^{2-}

Molecular orbital	O_2^+ $[O\overset{\cdots}{=}O]^+$	O_2 $[O\overset{\cdots}{\underset{\cdots}{:}}O]$	O_2^- $[O\overset{\cdots}{-}O]^-$	O_2^{2-} $[O-O]^{2-}$
σ_z^*	—	—	—	—
$\pi_x^*\pi_y^*$	↑ —	↑ ↑	↑↓ ↑	↑↓ ↑↓
$\pi_x\pi_y$	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓	↑↓ ↑↓
σ_z	↑↓	↑↓	↑↓	↑↓
σ_s^*	↑↓	↑↓	↑↓	↑↓
σ_s	↑↓	↑↓	↑↓	↑↓
Bond order	2.5	2	1.5	1
Intermolecular distance, nm	0.112	0.1207	0.132	0.149
Dissociation energy, kJ/mol	642	494	394	210

As will be seen from the table, the removal of an electron from the π^* orbital corresponds to an increased bond order in O_2^+, while the gain of electrons in the π^* orbital, on the contrary, reduces bond order in the O_2^{2-} and O_2^- molecular ions. In accordance with the diminishing bond order in the series $O_2^+—O_2—O_2^-—O_2^{2-}$ the distance between the oxygen atoms increases and average bond energy falls.

The addition of one electron to the O_2 molecule results in a *superoxide* O_2^- ion

$$:O\overset{\cdots}{\underset{\cdots}{:}}O: + e^- = [:\ddot{O}\overset{\cdots}{-}\ddot{O}:]^-$$

Derivatives of the O_2^- radical—*superoxides*—are known for the most active alkali metals (K, Rb, Cs). They are formed by the direct interaction of the simple substances

$$K + O_2 = KO_2$$

The presence of an unpaired electron in O_2^- accounts for the paramagnetism and colour of superoxides. They are very strong oxidants and react vigorously with water, liberating oxygen.

On gaining two electrons, the O_2 molecule is converted into an O_2^{2-} peroxide ion in which the atoms are linked by a single two-electron bond, so that it is diamagnetic:

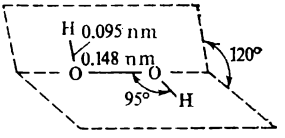
$$:\ddot{O}\overset{\cdot\cdot}{=}\ddot{O}: \xrightarrow{+2e^-} [:\ddot{O}-\ddot{O}:]^{2-}$$

This agrees with the absence of colour in *peroxides*.

Peroxides are formed during the oxidation of certain metals, e.g.

$$Ba + O_2 = BaO_2$$

The most important peroxide is that of hydrogen, H_2O_2. Its structure is shown below



The O—O bond energy is 210 kJ/mol, which is about half that of the H—O bond (468 kJ/mol).

Because of the asymmetrical distribution of H—O bonds the H_2O_2 molecule is strongly polarised ($\mu = 0.7 \times 10^{-29}$ C·m). The quite strong hydrogen bond arising between H_2O_2 molecules accounts for their association. In ordinary conditions hydrogen peroxide is a pale blue syrupy liquid (density 1.44 g/cc) with a comparatively high boiling point (b.p. 150.2 °C, f.p. 0.41 °C). It is a good ionising solvent and is miscible with water in any proportion owing to the formation of new hydrogen bonds. It can be isolated from solutions in the form of an unstable crystal hydrate $H_2O_2 \cdot 2H_2O$ (m.p. —52.0 °C). In the laboratory 3 per cent and 30 per cent (*perhydrol*) solutions are usually used.

Aqueous solutions of hydrogen peroxide are weak acids ($K_{a1} = 2.24 \times 10^{-12}$):

$$H_2O \ldots H_2O_2 \rightleftarrows OH_3^+ + \underset{\text{ion}}{\underset{\text{Hydroperoxide}}{HO_2^-}}$$

The peroxide radical can be transferred without alteration to other compounds in chemical reactions, e.g.

$$H_2O_2 + 2NaOH = Na_2O_2 + 2H_2O$$

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2$$

The second reaction is used to obtain hydrogen peroxide.

The reactions often, however, proceed with disruption of the O—O bond or a change in the charge of the O_2^{2-} ion, which can be considered to gain or lose electrons

$$O_2^{2-} + 2e^- = \overset{-2}{2O} \text{—oxidant}$$

$$O_2^{2-} - 2e^- = \overset{0}{O_2} \text{—reductant}$$

In the first case peroxides display oxidising properties and in the second reducing ones, for example,

$$2\overset{-1}{K}\overset{-1}{I} + \overset{(-2)}{Na_2O_2} + 2H_2SO_4 = \overset{0}{I_2} + Na_2SO_4 + K_2SO_4 + 2\overset{-2}{H_2O}$$

oxidant

$$2K\overset{+7}{Mn}O_4 + 5\overset{(-2)}{H_2O_2} + 3H_2SO_4 = 2\overset{+2}{Mn}SO_4 + 5\overset{0}{O_2} + K_2SO_4 + 8H_2O$$

Reductant

Peroxides' oxidising properties are stronger than their reducing properties:

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O, \quad E^\circ_{298} = 1.78 \text{ V}$$

$$O_2 + 2H^+ + 2e^- = H_2O_2, \quad E^\circ_{298} = 0.68 \text{ V}$$

Thus, the action of concentrated H_2O_2 on paper, sawdust, and other combustible materials leads to spontaneous combustion. Its reducing properties are only displayed with such strong oxidants as the MnO_4^- ion.

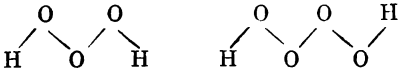
Decomposition by a disproportionation mechanism is also characteristic:

$$\overset{-1}{H_2O_2} + \overset{-1}{H_2O_2} = \overset{-2}{2H_2O} + \overset{0}{O_2}$$

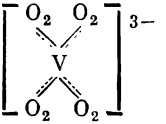
This is accelerated by the presence of admixtures, or by illumination or heating, and may be explosive. Only very pure H_2O_2 and 30-65 per cent solutions are quite stable. Hydrogen peroxide itself and solutions of it are usually stored in the cold and dark. Inhibitors are added to stabilise them.

Aqueous solutions of peroxide are widely used to bleach various materials and decontaminate effluents. It is also used as an oxidant in rocket fuels.

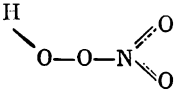
H_2O_3 and H_2O_4 have been recently synthesised. These are very unstable, decomposing at ordinary temperatures within fractions of a second. But at low temperatures, of the order of —70 °C, they can exist for hours. Spectroscopy reveals that their molecules have a zig-zag chain structure:



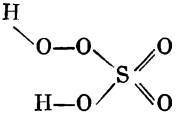
The molecules of H_2O_2, like those of H_2O, can act as neutral ligands, e.g. $[Fe(OH_2)_5(O_2H_2)]^{3+}$, and yield *peroxyhydrates* similar to crystal hydrates: viz., $K_2CO_3 \cdot 3H_2O_2$, $CaO_2 \cdot 2H_2O_2$, $BaO_2 \times \times 2H_2O \cdot 2H_2O_2$, etc. The peroxide ion can also act as a ligand as, for example, in the complex $[V(O_2)_4]^{3-}$



Acids containing the O_2^{2-} grouping are known as *peroxyacids*:



HNO_4
Peroxynitric acid



H_2SO_5
Peroxysulphuric acid

Hydrogen peroxide is liberated during the hydrolysis of peroxyacids, which is used to obtain it in industry.

The characteristic feature of peroxide compounds, both simple and complex, is their ability to form hydrogen peroxide in reaction with dilute solutions of acids and to liberate oxygen during thermal decomposition or the action of water and other chemical agents. Other inorganic compounds that can serve as sources of oxygen, like nitrates, chlorates, perchlorates, permanganates, and certain oxides, do not liberate hydrogen peroxide during reaction with water. They liberate oxygen only when heated or in the presence of catalysts.

Compounds of oxygen(II) and oxygen(I). It can be taken that an electropositive polarisation of the oxygen atoms is exhibited in its compounds with fluorine and in the O_2^+ ion. Examples of fluorine derivatives of oxygen compounds are given in Table 35.

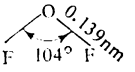
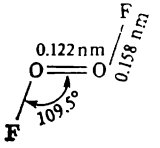
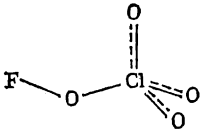
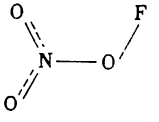
The simplest representative of these compounds is OF_2 oxygen *difluoride*, which is obtained by passing fluorine swiftly through a 2 per cent alkaline solution

$$2F_2 + 2NaOH = OF_2 + 2NaF + H_2O$$

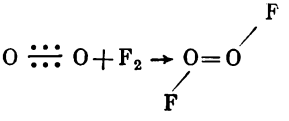
The OF_2 molecule is angular ($d_{OF} = 0.139$ nm, $\angle FOF = 104°16'$, $\mu = 0.1 \times 10^{-29}$ C·m). Oxygen difluoride is a poisonous, pale yellow gas, thermally stable at temperature below 200 to 250 °C; it is a strong oxidant and an effective fluorinating agent.

The O_2^{2+} radical in the *dioxydifluoride* O_2F_2 has covalent bonds with the fluorine atoms. The O_2F_2 molecule is diamagnetic. This compound is formed as a red volatile liquid by the direct interaction of the simple substances in an electric discharge or under the action of ionising radiation at the temperature of liquid air (—190 °C).

Table 35. Selected Compounds of Fluorine and Oxygen

Compound	Structure of molecule	$\mu \times 10^{-29}$, C·m	F.p., °C	B.p., °C	State of aggregation in ordinary conditions	ΔH_f°, 298, kJ/mol
OF_2		0.10	—224	—145	yellow gas	24.2
O_2F_2		0.48	—154	—57 (decomp.)	orangish-yellow gas	18
ClO_4F		—	—167	—15.9	colourless gas, explosive	77
NO_3F		—	—175	—45.9	ditto	10.5

Spectroscopically the O_2F_2 molecule ($\mu = 0.48 \times 10^{-29}$ C·m) has the structure similar to that of H_2O_2:



The compound is very unstable owing to the low energy of the OF bond rupture (75 kJ/mol).

Polyoxydifluorides of the type of O_4F_2, O_5F_2, and O_6F_2 have also been obtained. They exist only at low temperatures (—190 °C). It is supposed that their molecules have a chain structure, e.g. F/O\O/O\O/F. Their thermal stability decreases with an increasing number of atoms in the molecule O_nF_2 ($n = 2$ to 6).

The energy of ionisation of the O_2 molecule is quite considerable (12.08 eV) but, during the interaction with the very strong oxidant PtF_6, oxygen forms a salt-like substance $O_2^+[PtF_6]^-$

$$\underset{\text{Reductant}}{O_2} + PtF_6 = O_2^+[PtF_6]^-$$

in which the O_2^+ ion (*dioxygenyl*) acts as a cation

$$[\,O \overset{\cdots}{\equiv} O :]^+$$

Dioxygenyl hexafluoroplatinate(V), $O_2[PtF_6]$, is paramagnetic. It is a red substance melting and decomposing at 219 °C. Its synthesis in 1962 by the Canadian scientist N. Bartlett gave an impetus to the subsequent synthesis of compounds of xenon, whose ionisation energy is close to that of oxygen (see p 495).

Derivatives of O_2^+ have also been obtained by the interaction of O_2F_2 and O_4F_2 with pronouncedly acidic fluorides of the type BF_3, PF_5, AsF_5, SbF_5, and BrF_5:

$$O_2F_2 + PF_5 = O_2[PF_6] + 1/2\ F_2$$
$$O_4F_2 + 2BF_3 = 2O_2[BF_4]$$

Dioxygenyl salts can be synthesised by heating a mixture of oxygen, fluorine, and powder of the corresponding metal (in an autoclave for 10 to 20 hours at a temperature between 150 and 500 °C)

$$O_2 + 3F_2 + E = O_2^+[EF_6]$$

where E is As, Sb, Bi, Nb, Pt, Au, Ru, or Rh.

The frequency of the valence oscillations of O_2^+ in dioxygenyl compounds is close to that of the free ion, which points to its existence in said salts. The internuclear distance in the O_2^+ cation (known from spectroscopic findings) is 0.112 nm. As might be expected, it is shorter than in O_2 (0.1207 nm). The O_2^+ ion has one unpaired electron (see Table 34). The dissociation energy of O_2F_2, OF_2 (about 70 kJ/mol) is lower than that of F_2 (159 kJ/mol). These compounds are a convenient way of storing fluorine, which is liberated from them at normal temperatures.

In compounds of the type of ClO_4F and NO_3F one of the oxygen atoms is a bridge atom linking the central atom (Cl, N) and the fluorine atom. The compounds can be obtained by reacting fluorine with concentrated solutions of $HClO_4$ and HNO_3 or with solid $KClO_4$ and KNO_3:

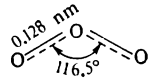
$$HClO_4 + F_2 = ClO_4F + HF$$
$$KNO_3 + F_2 = NO_3F + KF$$

They decompose in water, liberating oxygen

$$2ClO_4F + 2H_2O = 2HClO_4 + 2HF + O_2$$

Derivatives of positively polarised oxygen are very strong, powerful oxidants capable (in certain conditions) of liberating the chemical energy stored in them. They can therefore be used as effective oxidants of rocket fuel.

Compounds of oxygen(IV). The ozone O_3 ($\overset{+4}{O}O_2$) allotropic form of oxygen can be considered a derivative of O(IV). Its molecule is diamagnetic, has an angular configuration ($\angle OOO = 116.5°$), and possesses a certain polarity ($\mu = 0.17 \times 10^{-29}$ C·m). The bond length $d_{(OO)}$ (0.128 nm) is intermediate between the single bond (0.149 nm) and double bond (0.1207 nm). The bond order of the O_3 molecule is therefore taken as 1.5. The structure of ozone can be represented as follows



From the above data, we can explain this structure as follows. The central oxygen atom in the O_3 molecule is in the sp^2 hybridisation (through $2s$, $2p_x$, and $2p_z$ orbitals). Two of the hybrid sp^2 orbitals of the central atom are involved in the forming of two σ bonds O—O (two molecular σ orbitals). The third sp^2 hybrid orbital (molecular σ^{non} orbital) contains an unshared electron pair. The $2p_y$ orbital of the central atom (perpendicularly to the plane of the atoms) and $2p_y$ orbitals of the marginal atoms are involved in the formation of a delocalised π bond (molecular π orbital). Thus, the ground state of the ozone molecule corresponds to the following filling of molecular orbitals:

$$[\sigma]^4[\pi]^2[\sigma^{non}]^2$$

The other electrons fill nonbonding orbitals localised in the peripheral atoms (see Fig. 158 on p 366).

The six electrons bonding the three oxygen atoms correspond to a bond order of 1.5.

Ozone is a very toxic blue gas with a pungent, irritating odour. Liquid ozone is dark blue; in the solid state it is a dark violet crystalline substance (f.p. —192.7 °C). Its polarity and polarizability are higher than those of oxygen so that it boils at a higher temperature (—111.9 °C). This also accounts for its more intense colour and better solubility in water.

Ozone is formed in processes that are accompanied with the liberation of atomic oxygen (radiolysis of water, decomposition of peroxides, etc.), and by the action of electrons, protons, and short-wave radiation on molecular oxygen, i.e. by radiochemical and photochemical reactions. The chain reaction of formation of ozone can be represented as follows:

$$O_2 + h\nu \rightarrow O_2^*$$

$$O_2^* + O_2 = O_3 + \cdot O\cdot$$

$$\cdot O\cdot + O_2 = O_3$$

or, in summary form, as

$$3O_2 = 2O_3, \quad \Delta G^\circ_{298} = 325 \text{ kJ}$$

In natural conditions ozone is formed from oxygen during lightning discharges, and at altitudes of 10 000 to 30 000 metres through the action of solar ultraviolet radiation. Ozone removes harmful ultraviolet radiation from sunlight and also absorbs the Earth's own infrared radiation, thus protecting it against cooling. The ozone layer of the upper atmosphere consequently plays a major role in protecting life on Earth.

Industrially ozone is produced by silent electrical discharges in ozonisers.

Ozone is an endothermic substance ($\Delta H^\circ_{f,298} = 142$ kJ/mol, $\Delta G^\circ_{f,298} = 163$ kJ/mol), but in the absence of catalysts, or of ultraviolet radiation, gaseous ozone decomposes quite slowly, even at 250 °C. Liquid ozone and concentrated mixtures (70 per cent O_3) are explosive.

Ozone's oxidising power is much higher than that of oxygen. In ordinary conditions it can, for example, oxidise many simple substances of low activity (Ag, Hg, etc.):

$$8Ag + 2O_3 = 4Ag_2O + O_2$$

Its higher chemical activity (compared with oxygen) can also be demonstrated by comparing their oxidation-reduction potentials for aqueous solutions, e.g.:

$$O_3\ (g) + H_2O\ (l) + 2e^- = O_2\ (g) + 2OH^-\ (sol), \quad E^\circ_{298} = 1.24\ V$$
$$O_2\ (g) + 2H_2O\ (l) + 4e^- = 4OH^-\ (sol), \quad E^\circ_{298} = 0.401\ V$$

Reaction of ozone with a KI solution can be used for its quantitative determination:

$$2I^-\ (sol) + O_3\ (g) + H_2O\ (l) = I_2\ (s) + 2OH^-\ (sol) + O_2\ (g)$$

Its electron affinity is about 180 kJ/mol, so that it can turn into the *ozonide* ion O_3^-. Ozone reacts with the alkali metals to give *ozonides*:

$$K + O_3 = KO_3$$

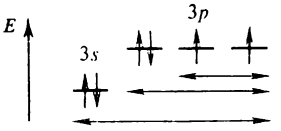
Ozonides are compounds consisting of positive metal ions and negative O_3^- ions ($d_{OO} = 0.134$ nm). The presence of an unpaired electron in the O_3^- ion explains the paramagnetism and colour of ozonides. As a rule they are red.

Being a strong oxidising agent, ozone is used to purify drinking water and disinfect air, and in various chemical syntheses.

4.2. Sulphur

The sulphur atom S, like that of oxygen, has six valence electrons ($3s^23p^4$). Sulphur is a typical nonmetal, and is second only to the halogens, oxygen, and nitrogen in electronegativity (its electronegativity is 2.5). Its most stable oxidation states are -2, $+2$, $+4$,

and +6, which is due to the involvement of two unpaired electrons and of one or two electron pairs in the formation of chemical bonds

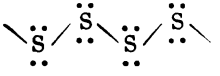


The lowest and the highest oxidation states are most characteristic of sulphur. As in the other *p* elements of the third period, its maximum coordination number is six, while the most stable coordination number is four (sp^3 hybrid state of orbitals). Sulphur compounds are known for almost all the elements.

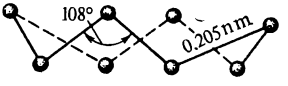
Sulphur is very common on Earth (0.03 mole per cent). It occurs in four natural isotopes: namely, ^{32}S (95.084 per cent), ^{33}S (0.74 per cent), ^{34}S (4.16 per cent) and ^{36}S (0.016 per cent). Beta-radioactive isotopes ^{31}S and ^{37}S have also been obtained artificially.

In accordance with its characteristic oxidation states, sulphur occurs in nature as sulphides (ZnS, HgS, PbS, Cu_2S, FeS_2, $CuFeS_2$, etc.) and sulphates ($Na_2SO_4 \cdot 10H_2O$, $CaSO_4 \cdot 2H_2O$, $BaSO_4$, etc.). It also occurs in the native condition.

The simple substances. Sulphur differs essentially from oxygen in its ability to form homochains (d_{SS} = 2.05 nm) of a zig-zag configuration



The most stable form of sulphur is the ring ('crown') molecule of S_8



In addition, molecules with closed (S_6, S_4) and open chains S_∞ are possible. In ordinary conditions, *rhombic* α-S (density, 2.07 g/cm³) and partly *monoclinic* β-S (density, 1.96 g/cm³) are stable. Their crystals are characterised by mutual orientation of S_8 rings.

The outward shapes of the rhombic and monoclinic crystals of sulphur are illustrated in Fig. 148. Rhombic sulphur is yellow and monoclinic sulphur a pale yellow. *Plastic* sulphur, which is not stable in normal conditions, consists of an irregular arrangement of zig-zag chains of S_∞ molecules (where ∞ may be as great as several thousands). Other unstable forms are built up of S_2 molecules (purple), S_6 molecules (orange-yellow), etc.

Monoclinic sulphur melts at 119.3 °C and rhombic sulphur at 112.8 °C, forming a highly mobile yellow liquid. At 160 °C, however, this liquid darkens and becomes more viscous, and at 200 °C becomes dark brown and as viscous as pitch, which is due to disruption of

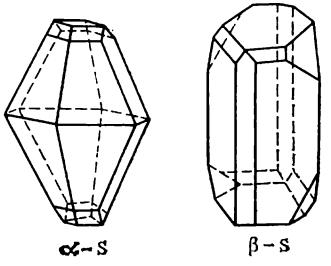


Fig. 148. The habit of crystals of rhombic (α-S) and monoclinic (β-S) sulphur

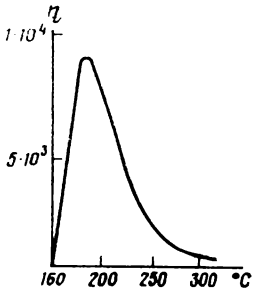


Fig. 149. Variation in relative sulphur viscosity ($\eta = 1$ at 160 °C) with temperature

the S_8 ring molecules and the formation of molecules in the shape of long chains of S_∞ consisting of hundreds of thousands of atoms. Further heating (above 250 °C) breaks these chains and the sulphur again becomes more mobile. Figure 149 shows variation in liquid sulphur viscosity with temperature (at 190 °C about 9000 times higher than at 160 °C).

Sulphur boils at 444.6 °C. Its vapour may contain S_8, S_6, S_4, and S_2 molecules, depending on the temperature. As the composition of the molecules alters, the colour of the sulphur vapour changes from orange-yellow to straw-yellow. At temperatures above 1500 °C S_2 molecules dissociate into atoms. S_2 molecules are paramagnetic and similar in structure to O_2 molecules. In all its other states sulphur is diamagnetic.

Sulphur is practically insoluble in water; some forms are soluble in organic solvents, in particular in carbon disulphide.

Sulphur is a quite active nonmetal. It begins to oxidise many simple substances even with moderate heating, but at the same time it easily oxidises by oxygen and the halogens. It undergoes disproportionation in boiling water and even more so in boiling solutions of alkalis:

$$\overset{0}{3S} + 6NaOH \rightleftharpoons \overset{-2}{2Na_2S} + \overset{+4}{Na_2SO_3} + 3H_2O$$

Sulphur is mainly obtained by melting native sulphur directly underground. It is used to produce sulphuric acid, to vulcanise rubber, and as an insecticide in agriculture, etc.

Compounds of sulphur (o.s. —2). The similarity between sulphur and oxygen is displayed most markedly in compounds in which their oxidation state is —2. Sulphides correspond to oxides, hydrosulphides to hydroxides, and thioacids to oxyacids, e.g.

	Na	Mg	Al	Si	P	S
Sulphide	Na_2S	MgS	Al_2S_3	SiS_2	P_2S_5	—
Oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3
Hydrosulphide	NaSH	$Mg(SH)_2$	$Al(SH)_3$	H_4SiS_4	H_3PS_4	—
Hydroxide	NaOH	$Mg(OH)_2$	$Al(OH)_3$	H_4SiO_4	H_3PO_4	H_2SO_4
Chemical nature of compounds	Basic		Amphoteric	Acidic		

As will be seen from these examples, the chemical nature of the related oxides and sulphides, hydroxides and hydrosulphides changes regularly within a period. Like oxides, sulphides may be basic, amphoteric, or acidic. Basic properties are characteristic of the sulphides of the most typical metals and acidic properties of the sulphides of nonmetals. The difference in their chemical nature is evident in solvolysis and in the interaction between sulphides of various chemical nature. Thus, the sulphides of Group I *s* elements (like their oxides) are soluble in water and form an alkaline medium on hydrolysis:

$$Na_2S + HOH \rightleftharpoons NaSH + NaOH$$

The sulphides of nonmetals usually hydrolyse irreversibly forming corresponding acids:

$$SiS_2 + 3H_2O = H_2SiO_3 + 2H_2S$$

Amphoteric sulphides (like amphoteric oxides) are insoluble in water, but some (e.g. the sulphides Al(III)) are completely hydrolysed:

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$$

The interaction of basic and acidic sulphides results in what are called thiosalts, e.g.

$$Na_2S + CS_2 = Na_2CS_3$$

Trisulphide carbonate(IV)

Thioacids are not usually stable and decompose irreversibly into H_2S and the corresponding sulphide. Thus, when sulphide carbonate reacts with acid, the resultant acid decomposes:

$$Na_2CS_3 + H_2SO_4 = Na_2SO_4 + H_2CS_3$$
$$H_2CS_3 = H_2S + CS_2$$

This decomposition is similar to that of oxyacids into the corresponding anhydride and water:

$$H_2CO_3 = H_2O + CO_2$$

Sulphides have characteristic colours, e.g. CuS, NiS, and PbS are black, MnS is flesh coloured, and ZnS is white. These different colours and solubilities in various media are employed in analytical chemistry to detect and separate cations.

The molecule of hydrogen sulphide H_2S has an angular configuration ($\angle HSH = 92°$, $d_{SH} = 0.133$ nm) and it is therefore polar ($\mu = 0.34 \times 10^{-29}$ C·m). The capacity of H_2S to form hydrogen bonds is less marked than that of H_2O, so that it is a gas in ordinary conditions (f.p. −85.6 °C, b.p. −60.75 °C). Its self-ionisation in the liquid state is negligible:

$$H_2S \cdots H_2S \rightleftharpoons SH_3^+ + SH^-$$

The ion product of hydrogen sulphide $[SH_3^+][SH^-] = 3 \times 10^{-33}$. H_2S ionises much better in water

$$H_2O \cdots H_2S \rightleftharpoons OH_3^+ + SH^-$$

The aqueous solution of H_2S is a weak acid ($K_{a1} = 1 \times 10^{-7}$) known as *hydrosulphuric* acid. Hydrogen sulphide has an offensive odour and is *very poisonous*. It is usually obtained by the action of dilute HCl on FeS. Insoluble sulphides are prepared by exchange reactions:

$$MnSO_4\ (sol) + Na_2S\ (sol) = MnS\ (s) + Na_2SO_4\ (sol)$$

$$CuSO_4\ (sol) + H_2S\ (sol) = CuS\ (s) + H_2SO_4\ (sol)$$

Sulphides are reductants in solutions:

$$S + 2e^- = S^{2-}, \quad E° = -0.48\ V$$

$$SO_4^{2-} + 8H^+ + 8e^- = S^{2-} + 4H_2O, \quad E° = 0.15\ V$$

The oxidation products may be S, SO_2 and H_2SO_4, depending on the conditions:

$$2K\overset{+7}{M}n\overset{-2}{O_4} + 5H_2\overset{-2}{S} + 3H_2SO_4 = 2\overset{+2}{M}nSO_4 + 5\overset{0}{S} + K_2SO_4 + 8H_2O$$

$$H_2\overset{-2}{S} + 4\overset{0}{Br_2} + 4H_2O = H_2\overset{+6}{S}O_4 + 8\overset{-1}{H}Br$$

The sulphides of metals, like their oxides, have a variable composition, e.g., $FeS_{1.01}$—$FeS_{1.14}$ (cf. $FeO_{1.04}$—$FeO_{1.12}$). Their physical properties (like those of oxides) are very diverse. Thus, TiS_2 has metallic conductivity, ZrS_2 is a semiconductor, and HfS_2 is a dielectric.

The colour of sulphides becomes stronger in the subgroups of the periodic system with increasing atomic number of the element, e.g.:

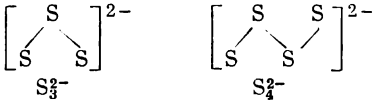
As_2S_3	yellow	ZnS	white	Ga_2S_3	yellow	GeS_2	white
Sb_2S_3	orange	CdS	yellow	In_2S_3	yellow	SnS_2	yellow
Bi_2S_3	black	HgS	black	Tl_2S_3	black	PbS	black

This phenomenon is due to the increasing share of the delocalised bond in sulphides.

Persulphides. Sulphur's tendency to form homochains is realised in many *persulphides* (polysulphides) of the type of $\overset{+1}{M}_2S_n$, which are obtained by reacting it with concentrated solutions of a basic sulphide:

$$Na_2S + (n - 1)S = Na_2S_n$$

Persulphide ions have a chain structure:



S_3^{2-} S_4^{2-}

Many hydrogen persulphides of the type of H_2S_n (*sulphanes* or polysulphides of hydrogen) have been obtained ($n = 2 \div 23$). They are oily yellow liquids (f.p. −50 to −90 °C).

As the sulphur content of persulphides increases, their colour changes from yellow (S_2^{2-} radical) to red (S_3^{2-} radical). A mixture of sulphanes is formed by the action of acids on polysulphides of ammonium or sodium:

$$Na_2S_n + 2HCl = H_2S_n + 2NaCl$$

Hydrogen persulphide H_2S_2 is an analogue of hydrogen peroxide. Persulphides occur in nature. The common mineral *pyrite* FeS_2, for example, is a persulphide of iron(II) (Fig. 150).

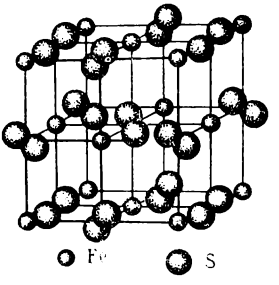


Fig. 150. Structure of pyrite FeS_2

Like peroxides, persulphides have both reducing and oxidising properties and also undergo disproportionation:

S_2^{2-}—oxidant $\quad \overset{(-2)\ +2}{Na_2S_2} + \overset{+4}{SnS} = \overset{-2}{SnS_2} + Na_2S$

S_2^{2-}—reductant $\quad \overset{+2\ (-2)}{4FeS_2} + \overset{0}{11O_2} = \overset{+3\ -2}{2Fe_2O_3} + \overset{+4\ -2}{8SO_2}$

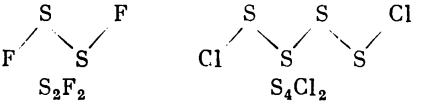
S_2^{2-}—oxidant-reductant $\quad \overset{(-2)}{Na_2S_2} = Na_2\overset{-2}{S} + \overset{0}{S}$

Compounds of sulphur(II). An oxidation state of +2 is not characteristic of sulphur yet it is more stable than that of oxygen. Unstable $SHal_2$ halide derivatives of sulphur(II) are known.

Sulphur dichloride SCl_2 is a dark red liquid that decomposes gradually

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

Halides of radicals like S_n^{2+} are more numerous, e.g.



S_2F_2 S_4Cl_2

The zig-zag chain can be very long (up to $S_{100}Cl_2$). Members of the series up to S_8Hal_2 have been isolated.

Halides of the S_nHal_2 type are oily red liquids with a disagreeable smell. The most stable are S_2Hal_2, which are similar to O_2F_2 in structure. The chloride S_2Cl_2 is obtained by chlorinating molten sulphur. It is mainly used as a solvent for many compounds and sulphur. When sulphur is dissolved, compounds up to $S_{100}Cl_2$ are formed, which are used to vulcanise rubber.

Compounds of sulphur(IV). A +4 oxidation state occurs in $SHal_4$ tetrahalides, $SOHal_2$ oxydihalides, the dioxide SO_2, and in the corresponding anions:

SF_4	$SOHal_2$	SO_2
$[SF_5]^-$	$[SO_2F]^-$	$[SO_3]^{2-}$

Information on selected sulphur(IV) compounds is given in Table 36. All these molecules, and anion complexes of sulphur(IV), have an unshared (nonbonding) electron pair in the sulphur atom. In accordance with the number of the sulphur atom's σ bonding and nonbonding electron pairs, $SHal_4$ molecules have the configuration of a distorted tetrahedron, $SOHal_2$ and SO_3^{2-} are trigonal pyramids, and SO_2 is an angular configuration, i.e. they belong to the compounds of the AB_4E, AB_3E, and AB_2E type respectively (see Fig. 51).

The binary compounds of sulphur(IV) are acidic as is shown by their relation to water:

$$SO_2 + H_2O = H_2SO_3$$
$$SF_4 + 3H_2O = H_2SO_3 + 4HF$$
$$SOCl_2 + 2H_2O = H_2SO_3 + 2HCl$$

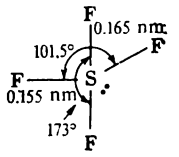
During hydrolysis they yield sulphurous acid (or rather HSO_3^- and SO_3^{2-} ions) or SO_2.

Sulphur dioxide SO_2 is the most important binary compound of sulphur(IV). Its structure is similar to that of the ozone molecule O_3 (OO_2) but its thermal stability is high (E_{SO} = 497 kJ/mol). In ordinary conditions it is a colourless gas with a specific pungent odour. It is made industrially by burning sulphur or roasting sulphide ores:

$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3$$

The solubility of sulphur dioxide in water is very high (about 40 volumes of SO_2 in one volume of water in ordinary conditions). The aqueous solution of SO_2 is *sulphurous acid*. The bulk of the dissolved SO_2 is present in solution as $SO_2 \cdot nH_2O$. When the solution

Table 36. **Selected Compounds of Sulphur(IV)**

Compound	Molecular structure	$\mu \times 10^{29}$, C·m	F.p., °C	B.p., °C	Physical state in normal conditions	$\Delta H^\circ_{f,298}$, kJ/mol	$\Delta G^\circ_{f,298}$, kJ/mol
Sulphur tetrafluoride, SF_4	 Distorted **tetrahedral**	0.21	—121	—38	Colourless gas	—770	—725.9
Sulphur difluoride oxide (thionyl fluoride), SOF_2		0.54	—129	—43	Colourless gas	—710	—694
Sulphur dichloride oxide (thionyl chloride), $SOCl_2$	**Pyramidal**	0.48	—104	+76	Colourless liquid	—247	—
Sulphur dibromide oxide (thionyl bromide), $SOBr_2$		0.49	—52	+138	Orange liquid	—	—
Sulphur dioxide, SO_2	**Angular**	0.53	—75.5	—10.0	Colourless gas	—296.9	—300.2

is cooled, a crystal hydrate of the clathrate type can be isolated (approximate composition, $SO_2 \cdot 7H_2O$). Only a few of the dissolved molecules react with water

$$SO_2 + H_2O \rightleftarrows H_2SO_3 \rightleftarrows H^+ + HSO_3^- \rightleftarrows 2H^+ + SO_3^{2-}$$

This equilibrium shifts readily toward the formation of HSO_3^- and SO_3^{2-} in the presence of alkali. Trioxysulphates(IV) of two types are formed, namely, $\overset{+1}{M}_2SO_3$ (*sulphites*) and $\overset{+1}{M}HSO_3$ (*hydrosulphites*):

$$NaOH + SO_2 = NaHSO_3$$

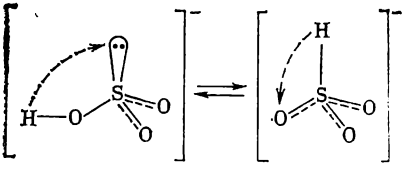
$$2NaOH + 2SO_2 = Na_2SO_3 + H_2O$$

Salts of Group I *s* elements and hydrosulphites like $\overset{+2}{M}(HSO_3)_2$ are soluble only in water. Insoluble sulphites are prepared by exchange reactions:

$$Na_2SO_3\ (sol) + CuSO_4\ (sol) = CuSO_3\ (s) + Na_2SO_4\ (sol)$$

Because of the instability of H_2SO_3, the action of acids on sulphites is accompanied with liberation of SO_2, which is widely used in the laboratory to prepare SO_2.

The SO_3^{2-} ion has the structure of a trigonal pyramid with the sulphur atom at the apex (see Fig. 51*d*). The unshared electron pair of the sulphur atom is space directional so that the SO_3^{2-} ion is an active donor of an electron pair and is easily transformed into tetrahedral HSO_3^- and SO_4^{2-} ions. The HSO_3^- ion exists in the form of two interconvertible isomers:



The phenomenon of reversible isomerism, in which two or more isomers change into one another, is called *tautomerism*. Derivatives of both tautomeric forms of the HSO_3^- ion have been obtained.

The ease with which the SO_3^{2-} ion is converted into the SO_4^{2-} ion accounts for its quite strong reducing properties:

$$SO_4^{2-} + H_2O + 2e^- = SO_3^{2-} + 2OH^-, \qquad E^\circ_{298} = -0.93\ V$$

Sulphites, for example, are therefore gradually oxidised in solution even by molecular atmospheric oxygen:

$$2SO_3^{2-} + O_2 = 2SO_4^{2-}$$

Reducing properties are also displayed by SO_2 which is oxidised, for example, by chlorine on exposure to sunlight

$$\overset{+4}{S}O_2 + \overset{0}{Cl_2} = \overset{+6}{S}O_2\overset{-1}{Cl_2}$$

Derivatives of sulphur(IV) display oxidising properties in reactions with stronger reductants:

$$\overset{+4}{S}O_2 + 2H_2\overset{-2}{S} = 3\overset{0}{S} + 2H_2O$$

When heated, sulphites undergo disproportionation

$$4Na_2\overset{+4}{S}O_3 = 3Na_2\overset{+6}{S}O_4 + Na_2\overset{-2}{S}$$

Sulphur dioxide is used to produce sulphuric acid and as a bleaching agent in the making of paper and in textile industry, to preserve

fruits, etc. Liquid SO_2 is used as a nonaqueous solvent for varioua syntheses. Sulphur(IV) oxydichloride $SOCl_2$ is used for the same purpose.

Compounds of sulphur(VI). A +6 oxidation state is displayed in the hexafluoride SF_6, trioxide SO_3, dioxydihalides SO_2Hal_2, and in the corresponding $[SO_4]^{2-}$, $[SO_3Hal]^-$ anion complexes and certain others:

SF_6	SOF_4	SO_2Hal_2	SO_3
—	—	$[SO_3Hal]^-$	$[SO_4]^{2-}$

Data on selected derivatives of sulphur(VI) are given in Table 37.

In ordinary conditions sulphur(VI) fluoride is a gas and sulphur(VI) oxyhalides are liquids or gases. Like SO_3, they are typical acidic compounds, most of them readily hydrolysed to form acids:

$$SO_3 + H_2O = 2H^+ + SO_4^{2-}$$

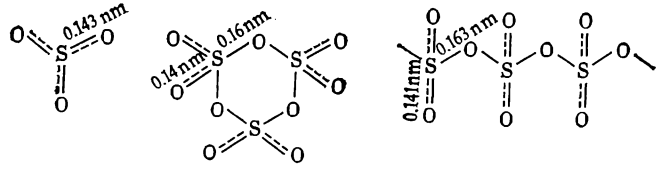
$$SO_2Cl_2 + 2H_2O = 4H^+ + SO_4^{2-} + 2Cl^-$$

The molecule of sulphur hexafluoride SF_6 is highly symmetrical, having the form of an octahedron with the sulphur atom at the centre. The hexafluoride is very stable chemically. It does not react with water, alkalis, or acids although the hydrolysis of SF_6 in solutions is characterised by high negative ΔG values, for example:

$$SF_6\ (g) + 3H_2O\ (g) = SO_3\ (g) + 6HF\ (g), \qquad \Delta G^\circ_{298} = -460\ kJ$$

The low reactivity of SF_6 is due to kinetic factors governed by the valence and coordinational saturation of the central atom of the molecule and its high ionisation energy (19.3 eV). SF_6 is a dielectric. Because of its chemical inertness and high molecular mass it is used as a gaseous insulator in high-voltage generators and other electrical apparatus. SO_2F_2 is also quite inactive, being decomposed only by alkaline solutions.

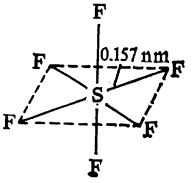
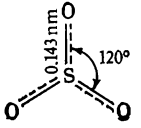
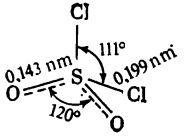
Since the coordination number 4 is most typical of sulphur(VI), the SO_3 molecule is easily polymerised into rings or open zig-zag polymer chains:



SO_3 Monomer — $(SO_3)_3$ Trimer — $(SO_3)_\infty$ Polymer

Sulphur trioxide therefore exists in several forms. When its vapour is condensed, a volatile liquid is formed that boils at 44.8 °C and consists mainly of cyclic trimeric molecules $(SO_3)_3$. When cooled to

Table 37. Selected Compounds of Sulphur(VI)

Compound	Structure of the molecule	$\mu \times 10^{29}$, C·m	F.p., °C	B.p., °C	Physical state in normal conditions	$\Delta H^\circ_{f,298}$, kJ/mol	$\Delta G^\circ_{f,298}$, kJ/mol
Sulphur hexafluoride, SF_6	 Octahedral	0	—50.7	—64	Colourless gas	—1207	1103
Sulphur trioxide, SO_3	 Triangular	0	—	—	Exists only as a vapour	—396	—370
Sulphur dioxydichloride (sulphuryl chloride), SO_2Cl_2	 Distorted tetrahedral	0.6	—54	+69.3	Colourless liquid	—391	—305
Sulphur dioxydifluoride (sulphuryl fluoride), SO_2F_2	Ditto	0.37	—136	—55	Colourless gas	—857	—811

16.8 °C it solidifies into a transparent mass resembling ice. The *ice-like form* γ-SO_3 alters during storage to a form resembling asbestos in appearance. The *asbestos-like form* α-SO_3 consists of zig-zag chains $(SO_3)_\infty$ of various length. Because of the heterogeneity of its composition, it has no definite melting point.

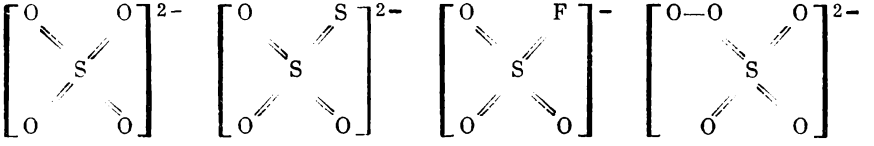
The structural features of these forms of sulphur trioxide account for the differences in their physical properties and chemical activity. Thus, the asbestos-like form, in contrast to the ice-like one, is less volatile and reacts less actively with water.

Sulphur trioxide is produced industrially by oxidising SO_2 in the presence of a catalyst (platinum, or oxides of vanadium).

Tetrahedral σ bonds of sulphur(VI) arise also during the interaction of SO_3 and certain hydrogen compounds, e.g. water and gaseous HF, HCl, and H_3N

$$H_2O + SO_3 = H_2[SO_4] \qquad HCl + SO_3 = H[SO_3Cl]$$
$$HF + SO_3 = H[SO_3F] \qquad H_3N + SO_3 = H[SO_3NH_2]$$

All the many sulphate(VI) complexes have a tetrahedral configuration



SO_4^{2-} — Tetraoxysulphate; SO_3S^{2-} — Sulphidetrioxysulphate; SO_3F^- — Fluorotrioxysulphate; $SO_3(O_2)^{2-}$ — Peroxytrioxysulphate

Hydrogen tetraoxysulphate(VI) H_2SO_4 is an oily liquid freezing at 10.4 °C. It is obtained by cooling concentrated sulphuric acid. The molecules of H_2SO_4 are linked by hydrogen bonds in both the liquid and the solid state. Liquid H_2SO_4 is an ionising solvent. Its own ionisation is insignificant and is expressed by the following equation

$$H_2SO_4 \cdots H_2SO_4 \rightleftharpoons SO_4H_3^+ + HSO_4^-, \quad K = 2.7 \times 10^{-4}$$

The aqueous solution of H_2SO_4 is a strong dibasic acid ($K_{a_1} = 1 \times 10^3$, $K_{a_2} = 1.2 \times 10^{-2}$).

The hydration of H_2SO_4 is accompanied with liberation of large quantities of heat, so that great care has to be taken when mixing it with water; the sulphuric acid should be added to the water in a thin stream and never water to the acid. Concentrated H_2SO_4 absorbs water vapour and for that reason is used as a drier or dehumidifier. It also extracts water from organic substances, charring them. When cooled, dilute sulphuric acid precipitates crystal hydrates (see Fig. 82).

Concentrated (98 per cent) sulphuric acid is obtained industrially by dissolving SO_3 in dilute H_2SO_4.

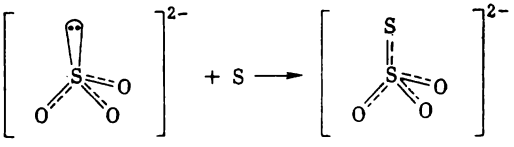
Most sulphates(VI) are readily soluble in water, but the tetraoxysulphates of Ba(II), Sr(II) and Pb(II) are poorly so. Sulphates(VI) are isolated from aqueous solutions as crystal hydrates. Compounds of the type of $CuSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ are known as *vitriols*.

Anhydrous tetraoxysulphates are obtained by the interaction of SO_3 and corresponding chlorides in nonaqueous media, for example, in liquid SO_2 or SO_2Cl_2:

$$CuCl_2 + 2SO_3 = CuSO_4 + SO_2Cl_2$$

Hydrogen trioxyfluorosulphate $H[SO_3F]$ (*fluorosulphonic acid*) and hydrogen trioxychlorosulphate $H[SO_3Cl]$ (*chlorosulphonic acid*) are liquids. Then aqueous solution of $H[SO_3F]$ is a very strong acid (like $HClO_4$) that slowly hydrolyses in water; $H[SO_3Cl]$ hydrolyses very energetically.

When a solution of sodium trioxysulphate(IV) is boiled with flowers of sulphur, sodium sulphide trioxysulphate(VI), usually known as sodium thiosulphate, is formed



The properties of *thiosulphates* depend on the particular oxidation state of the sulphur (+6 and —2). Thus, the presence of $\overset{-2}{S}$ is responsible for the reducing properties of the SO_3S^{2-} ion:

$$\overset{-2}{Na_2SO_3S} + \overset{0}{Cl_2} + H_2O = Na_2SO_4 + \overset{0}{S} + 2\overset{-1}{HCl}$$

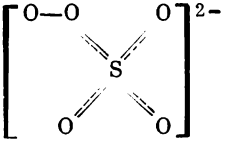
Hydrogen thiosulphate H_2SO_3S is unstable and decomposes the moment it is formed:

$$Na_2SO_3S + H_2SO_4 = Na_2SO_4 + H_2SO_3S$$

$$\overset{+6\ -2}{H_2SO_3S} = \overset{+4}{H_2SO_3} + \overset{0}{S}$$

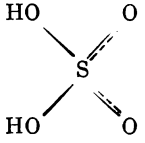
The most important thiosulphate is $Na_2S_2O_3 \cdot 3H_2O$, which is used in photography (where it is known as 'hypo') and in medicine.

The peroxide radical O_2^{2-} may be a ligand in the sulphate(VI) ion



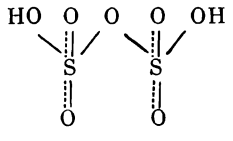
Derivatives of $[SO_3(O_2)]^{2-}$ ion (SO_5^{2-}) are called *peroxysulphates*(VI) and a solution of H_2SO_5 *peroxymonosulphuric* (or permonosulphuric) acid.

Like the oxide of sulphur(VI), sulphate complexes can also be polymers built of SO_4 tetrahedral structural cells. When SO_3 is dissolved in concentrated sulphuric acid, a series of *polysulphuric* acids is formed



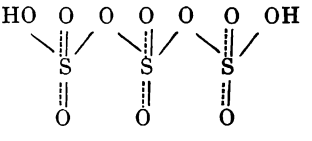
H_2SO_4

Hydrogen sulphate (sulphuric acid)



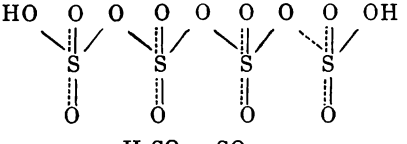
$H_2S_2O_7$

Hydrogen disulphate (disulphuric acid)



$H_2S_3O_{10}$

Hydrogen trisulphate (trisulphuric acid)

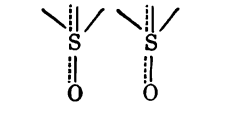


$H_2SO_4 \cdot nSO_3$

Hydrogen polysulphate (polysulphuric acid)

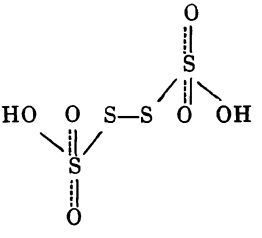
The mixture of H_2SO_4, $H_2S_2O_7$, $H_2S_3O_{10}$, and $H_2S_4O_{13}$ is a thick oily liquid fuming in air (*oleum*), widely used in industry. The S—O—S bond is broken by the action of water and the polysulphuric acids are converted into sulphuric acid.

The tetrahedral unit cells can unite in sulphates through the sulphur atom or a chain of sulphur atoms:



$H_2S_2O_6$

Hydrogen sulphidodisulphate (trisulphonic acid)

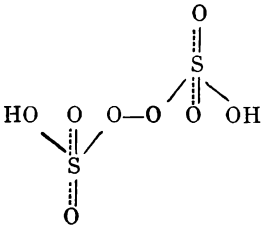


$H_2S_4O_6$

Hydrogen persulphidodisulphate (tetrathionic acid)

Compounds with the general formula $H_2S_xO_6$ ($x = 3$ to 6) are called *polythionic* acids.

Peroxide atom grouping can also act as a bridge uniting the tetrahedral unit cells:



$H_2S_2O_8$

Hydrogen peroxydisulphate
(peroxydisulphuric acid)

Peroxydisulphuric acid $H_2S_2O_8$ is prepared by electrolysis of sulphuric acid or hydrosulphates. The following reaction occurs at the anode

$$2HSO_4^- - 2e^- = H_2S_2O_8$$

Peroxydisulphuric acid $H_2S_2O_8$ and peroxymonosulphuric acid H_2SO_5 hydrolyse, forming hydrogen peroxide:

$$H_2S_2O_8 + 2H_2O = 2H_2SO_4 + H_2O_2$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2$$

This process is used in industry to prepare H_2O_2.

Peroxysulphates(VI) are strong oxidants and are used in chemical analysis and synthesis. Peroxysulphuric acids char paper, sugar, and even paraffin wax.

4.3. The Selenium Subgroup

Selenium (Se), tellurium (Te), and polonium (Po) are *p* elements with an s^2p^4 configuration of the valence electrons.

The unpaired electrons and one or two electron pairs are involved in the formation of bonds in selenium and its analogues. Odd oxidation numbers are therefore observed with Group VI *p* elements, viz., -2, $+2$, $+4$, and $+6$.

As in the other subgroups of *p* elements, there is a general tendency in the selenium subgroup to an increase in the characteristic coordination number. While the most typical coordination numbers for sulphur and selenium are 3 and 4, for tellurium they are 6, and sometimes even 7 and 8.

A secondary periodicity is clearly seen in the changing properties of compounds in the S—Se—Te—Po series in the highest oxidation state (see Fig. 137).

Selenium and tellurium are scattered elements and polonium a rare element (see Table 25). Natural selenium is a mixture of six stable isotopes, while tellurium consists of seven isotopes. Radioactive isotopes of selenium and tellurium have also been obtained. Polonium has no stable isotope but over twenty radioactive isotopes are known.

Minerals of selenium and tellurium are seldom encountered; most often they are present in free sulphur and sulphide ores (as selenides and tellurides). Polonium is contained in thorium and uranium minerals (as a product of the radioactive decay of the uranium radioactive series).

The simple substances. The type of stable molecule varies in the O—S—Se—Te—Po series from diatomic (oxygen O_2) through the cyclic S_8 and Se_8 molecules and Se_∞ and Te_∞ chain molecules to the metallic crystal of polonium.

Selenium, like sulphur, has polymorphic modifications. The most stable is hexagonal, or grey, selenium, the crystals of which are formed by zig-zag Se_∞ chains (Fig. 151). When liquid selenium is rapidly cooled a reddish-brown vitreous form is obtained, formed of randomly arranged Se_∞ molecules of various length. The crystalline forms of red selenium consist of Se_8 ring molecules (similar to S_8 molecules).

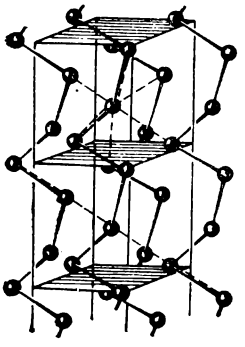


Fig. 151. Structure of hexagonal selenium and tellurium

Grey selenium is a semiconductor (ΔE = = 1.8 eV). Its electrical conductivity rises steeply (approximately 1000 times) with illumination. Liquid selenium also exhibits semiconductor properties.

Stable modifications of *tellurium* are formed by zig-zag Te_∞ molecules. The hexagonal form (see Fig. 151) is a silvery white, metal-like crystalline solid, brittle, and easily powdered. Its electrical conductivity is insignificant but increases with illumination, i.e. tellurium is a semiconductor ($\Delta E = 0.35$ eV). Amorphous (brown) tellurium is less stable than amorphous selenium and it is converted into the crystalline form at 25 °C.

Being isomorphic, hexagonal selenium and tellurium form a continuous series of solid solutions with one another. At high temperatures their vapours consist of paramagnetic Se_2 and Te_2 molecules. As the temperature falls, they are polymerised into E_4, E_6 and E_8 molecules.

Polonium is a silvery white, soft metal resembling bismuth and lead in its physical properties.

The structural changes in the O—S—Se—Te—Po series thus correspond to changes in physical properties: oxygen and sulphur are dielectrics, selenium and tellurium semiconductors, while polonium has metallic conductivity.

Certain constants of the simple substances of *p* elements of group VI are given below

	O_2	S (rhombic)	Se (hexagonal)	Te (hexagonal)	Po
Density, g/cm³	1.27*	2.07	4.82	6.25	9.3
M. p., °C	−219	119	217	450	246
B. p., °C	−183	445	685	990	962
S°_{298}, J/K·mol	205.04	31.9	42.1	49.50	—
ΔE, eV	—	—	1.8	0.35	(metal)
E°_{298}, $E+2H^+ + 2e^- = H_2E$, V	1.23	0.17	−0.40	−0.72	—

Oxidising activity decreases and reducing activity increases in the series O—S—Se—Te—Po, which is clear, for example, from comparison of their electrode potentials. The decrease in oxidising activity can be judged from the character of the changes in ΔG of analogous reactions involving the simple substances under consideration. Thus, the Gibbs' free energy in the reaction $H_2 + E = H_2E$ changes as follows

	H_2O (g)	H_2S (g)	H_2Se (c)	H_2Te (g)
ΔG°_f, kJ/mol	−229	−34	+20	+85

Selenium does not react with dilute acids or water, but tellurium is oxidised by water (at 100-160 °C)

$$Te + 2H_2O = TeO_2 + 2H_2$$

Polonium reacts with hydrochloric acid like a typical metal

$$Po + 2HCl = PoCl_2 + H_2$$

Like other nonmetals, Se and Te are oxidised to the corresponding acids by concentrated HNO_3 while polonium forms salt-like compounds:

$$Po + 8HNO_3 = Po(NO_3)_4 + 4NO_2 + 4H_2O$$

When selenium or tellurium is boiled in alkaline solutions it undergoes disproportionation like sulphur

$$\overset{0}{3E} + 6KOH = \overset{+4}{K_2EO_3} + 2\overset{-2}{K_2E} + 3H_2O$$

When heated, selenium and tellurium are quite readily oxidised by oxygen and the halogens; when melted they react with metals.

Selenium and tellurium are obtained by processing the wastes accumulated in dust traps during the production of sulphuric acid, and from the anode mud deposited during electrolytic refining of

* In the solid state.

nonferrous metals. The wastes and mud are oxidised, for example, by MnO_2; the resulting SeO_2 and TeO_2 are then separated and reduced with sulphuric dioxide:

$$EO_2 + 2SO_2 = E + 2SO_3$$

The polonium isotope ^{210}Po is produced by bombarding natural bismuth with neutrons:

$$^{209}Bi(n, \gamma)^{210}Bi \xrightarrow{-\beta^-} {}^{210}Po$$

Selenium and tellurium are used as semiconductors in photoelectric cells, optical and signalling instruments. Selenium is also used in the glass industry to make glass of ruby shades. The ^{210}Po isotope ($T_{1/2}$ = 138.4 days) is used as a source of alpha-particles.

Compounds of selenium (o.s. —2), tellurium (o.s. —2) and polonium (o.s. —2). A — 2 oxidation state is displayed in selenium, tellurium, and polonium in *selenides*, *tellurides*, and *polonides*, i.e. in compounds that are less electronegative than the elements themselves. There is a marked analogy with oxygen and sulphur in these compounds: for example,

oxides:	H_2O	Na_2O	CO_2
sulphides:	H_2S	Na_2S	CS_2
selenides:	H_2Se	Na_2Se	CSe_2
tellurides:	H_2Te	Na_2Te	CTe_2

In their crystal structure, solubility, and chemical properties, and in the methods of obtaining them, selenides and tellurides are similar to sulphides. They include basic (K_2Se, K_2Te) and acidic (CSe_2, CTe_2) compounds:

$$\underset{\text{Basic}}{K_2Se} + H_2O \rightleftharpoons KSeH + KOH; \quad \underset{\text{Acidic}}{CSe_2} + 3H_2O = H_2CO_3 + 2H_2Se$$

Because of the large size and low electronegativity of $\overset{-2}{Se}$ and $\overset{-2}{Te}$ atoms, they seldom act as ligands, so that complexation reactions between selenides, and even more so between tellurides, of different chemical nature are not characteristic.

The tendency to form compounds of an intermetallic type increases in the O—S—Se—Te—Po series with increasing metallic character of the simple substances. A big group of selenides and tellurides are semiconductors; those most used are the selenides and tellurides of elements of the zinc subgroup.

Hydrogen selenide H_2Se and hydrogen telluride H_2Te are gases in normal conditions. They have offensive odour and resemble H_2S

in their properties:

	H_2O	H_2S	H_2Se	H_2Te
M. p., °C	0	−85.6	−65.7	−51
B. p., °C	100	−60.4	−41.4	−2
d_{EH}, nm	0.096	0.133	0.146	0.169
E_{EH}, kJ/mol	463	347	276	238
∠ HEH	104.5°	92.2°	91.0°	90°
$\Delta H^\circ_{f,\,298}$, kJ/mol	−285.8	−21	33	99.7
$\Delta G^\circ_{f,\,298}$, kJ/mol	−237.24	−33.8	19.7	85.2
K_{a1}, in aqueous solution	1.8×10^{-16}	1×10^{-7}	1.7×10^{-4}	1.0×10^{-3}

As will be seen from this table, the stability of the molecule in the H_2O—H_2S—H_2Se—H_2Te series falls with increasing bond length and decreasing bond energy. Unlike the oxide and sulphide of hydrogen (H_2O and H_2S), hydrogen selenide and hydrogen telluride are endothermic ($\Delta H^\circ_f > 0$). When heated, H_2Te quickly decomposes, while H_2Po decomposes as soon as formed. Hydrogen telluride and hydrogen selenide can be obtained by the action of water or acid on selenides and tellurides of certain metals, e.g.

$$Al_2Te_3 + 6H_2O = 2Al(OH)_3 + 3H_2Te$$

H_2Se and H_2Te are more soluble in water than H_2S. Their solutions are acids. As will be seen from their ionisation constants, acid strength rises in the H_2O—H_2S—H_2Se—H_2Te series, which is due to the decreasing EH bond energy. The reducing activity of H_2E increases in this series.

Hydrogen selenide and its derivatives are *poisonous*!

Compounds of selenium(II), tellurium(II) and polonium(II). The derivatives of Se(II), Te(II), and Po(II) best studied are the halides. The relative stability of E(II) compounds increases in the O—S—Se—Te—Po series. While halides of the E_2Hal_2 type are typical of S and Se, they are unknown for tellurium and polonium, which form stable dihalides of the type $TeHal_2$ and $PoHal_2$. The halides of Se(II) are halogen anhydrides; the analogous derivatives of Te(II), and especially of Po(II), resemble salts in their properties.

Disproportionation of the halides during heating or hydrolysis are characteristic of the chemistry of Se(II) and Te(II)

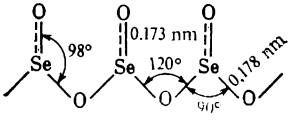
$$2\overset{+2}{Te}Cl_2 = \overset{+4}{Te}Cl_4 + \overset{0}{Te}$$

$$2\overset{+2}{Se}Cl_2 + 3H_2O = \overset{0}{Se} + H_2\overset{+4}{Se}O_3 + 4HCl$$

Compounds of selenium(IV), tellurium(IV) and polonium(IV). Selenium, tellurium, and polonium exhibit an oxidation state of +4 in the dioxides EO_2, tetrahalides $EHal_4$, oxydihalides $EOHal_2$, and in anion complexes of the $[EO_3]^{2-}$ and $[EHal_6]^{2-}$ type. Salt-like compounds of the $Po(SO_4)_2$ and $Po(NO_3)_4$ type are also characteristic of polonium(IV).

In contrast to sulphur, the *dioxides* of selenium and its analogues (EO_2) are polymers in normal conditions.

Thus, SeO_2 (sublimes at 315 °C) has a chain structure corresponding to sp^3 hybridisation of the selenium atom:



Tellurium dioxide TeO_2 (m.p. 733 °C) has a rutile structure (see Fig. 70*b*), i.e. its coordination number is six. The yellow form of PoO_2 (sublimes at 885 °C) has a cubic lattice of the CaF_2 type (see Fig. 70*a*) with a polonium coordination number of 8.

Acidic properties distinctly weaken in the series SeO_2—TeO_2—PoO_2. Thus, SeO_2 is readily soluble in water, forming *selenious acid* H_2SeO_3:

$$SeO_2 + H_2O = H_2SeO_3$$

Tellurium dioxide is insoluble in water but reacts with alkaline solutions

$$TeO_2 + 2KOH = K_2TeO_3 + H_2O$$

Polonium dioxide reacts with alkali only when melted, and reacts with acids as a basic oxide:

$$PoO_2 + 2H_2SO_4 = Po(SO_4)_2 + 2H_2O$$

Derivatives of EO_3^{2-} are known as *selenites*, *tellurites* and *polonites*.

Unlike H_2SO_3, hydrogen trioxyselenate(IV) H_2SeO_3 can be isolated in the free state. It is a white, solid substance easily giving up its water (at 70 °C). H_2TeO_3 is liable to polymerisation, so that a precipitate of varying composition $TeO_2 \cdot nH_2O$ is isolated by the action of acids on tellurites.

Apart from liquid SeF_4, the other *tetrahalides* are solids melting at 100 to 350 °C. They are formed by interaction of the simple substances. Being acidic, $EHal_4$ are quite easily hydrolysed (in particular $SeHal_4$)

$$SeCl_4 + 3H_2O = H_2SeO_3 + 4HCl$$

and react with basic halides

$$2KI + TeI_4 = K_2[TeI_6], \quad 2KCl + PoCl_4 = K_2[PoCl_6]$$

Complex halides of selenium(IV) and its analogues have a $\overset{+1}{M}[EHal_5]$ and $\overset{+2}{M}[EHal_6]$ composition. The $[EHal_5]^-$ ions are isostructural to IF_5 (see Fig. 51*f*). Complex halides are also formed by the reaction of EO_2 with concentrated hydrohalic acids:

$$TeO_2 + 6HI = H_2[TeI_6] + 2H_2O$$

The oxidising properties of the dioxide SeO_2 (and of SeO_3^{2-}) are stronger than their reducing properties compared with SO_2 (and SO_3^{2-}); for example, SeO_2 readily oxidises SO_2:

$$2SO_2 + SeO_2 = Se + 2SO_3$$

while stronger oxidants are required to oxidise E(IV) derivatives.

Compounds of selenium(VI), tellurium(VI) and polonium(VI). Binary compounds with oxygen and fluorine are known for selenium(VI) and tellurium(VI):

SeO_3	TeO_3	SeF_6	TeF_6
SeO_4^{2-}	TeO_6^{6-}	—	TeF_7^-

Compounds of polonium(VI) are unstable.

Like SO_3, selenium *trioxide* SeO_3 (m.p. 118.5 °C, decomposes at >185 °C) is white and is known in vitreous and asbestos-like forms. It reacts very vigorously with water to form *selenic* acid.

Tellurium trioxide TeO_3 also has two forms. It is practically insoluble in water but reacts with alkalis. Selenium trioxide SeO_3 is obtained by the action of SO_3 on selenates(VI) while TeO_3 is obtained by dehydrating hydrogen hexaoxytellurate(VI):

$$K_2SeO_4 + SO_3 = K_2SO_4 + SeO_3, \quad H_6TeO_6 = TeO_3 + 3H_2O$$

Tetraoxyselenates resemble tetraoxysulphates in composition, crystalline structure, and solubility. They are obtained by oxidising selenium in its lower oxidation states in an alkaline medium:

$$\overset{-2}{K_2Se} + 4\overset{+5}{NaNO_3} \xrightarrow{\text{fusion}} \overset{+6}{K_2SeO_4} + 4\overset{+3}{NaNO_2}$$

Hydrogen tetraoxyselenate(VI) H_2SeO_4 is a white crystalline solid (m.p. 62.4 °C). Like H_2SO_4, it avidly takes up water and chars organic substances. Its aqueous solution is a strong acid, known as selenic acid ($K_{a1} = 1 \times 10^3$, $K_{a2} = 1.2 \times 10^{-2}$). Crystal hydrates (oxonium selenates) of the following composition are precipitated from solutions: $H_2SeO_4 \cdot H_2O$, $H_2SeO_4 \cdot 2H_2O$, $H_2SeO_4 \cdot 4H_2O$.

The stable coordination number (with respect to oxygen) of tellurium is six (like that for the other *p* elements of the fifth period). Derivatives of the TeO_6^{6-} hexaoxytellurate complex are formed by fusing Te(IV) derivatives with alkalis in the presence of oxidants.

Hydrogen hexaoxytellurate (VI) H_6TeO_6 is a white crystalline solid readily soluble in hot water. Telluric acid is very weak ($K_{a1} = 2 \times 10^{-8}$, $K_{a2} = 5 \times 10^{-11}$). Its neutralisation with alkali gives hydrotellurates, e.g., $\overset{+1}{M}[TeO(OH)_5]$, $(\overset{+1}{M}H_5TeO_6)$, $\overset{+1}{M}_2[TeO_2(OH)_4]$, $(\overset{+1}{M}_2H_4TeO_6)$. Derivatives of the type Ag_6TeO_6 and Hg_3TeO_6 have also been prepared.

Other selenates(VI) and tellurates(VI), e.g. $H[SeO_3Cl]$ and $H[TeOF_5]$, are strong acids (in aqueous solutions). They are gradually hydrolysed.

Hexafluorides SeF_6 (sublimes at −46.6 °C) and TeF_6 (sublimes at −38.6 °C) are colourless gases. Their molecules are octahedral. Tellurium hexafluoride is more easily hydrolysed than SF_6 and SeF_6 which is explained by the coordination nonsaturation of tellurium

$$TeF_6 + 6H_2O = H_6TeO_6 + 6HF$$

For the same reason TeF_6 gives fluorotellurates(VI); e.g. $Cs_2[TeF_8]$ and $Ba[TeF_7]_2$.

The compounds of selenium(VI) are less stable (see Fig. 137) than the corresponding sulphur(VI) ones. Thus, SeO_3 and H_2SeO_4 decompose on heating with liberation of oxygen. H_2SeO_4 is therefore a stronger oxidant than H_2SO_4:

$$SeO_4^{2-} + 4H^+ + 2e^- = H_2SeO_3 + H_2O, \quad E^\circ = 1.15 \text{ V}$$
$$SO_4^{2-} + 4H^+ + 2e^- = H_2SO_3 + H_2O, \quad E^\circ = 0.17 \text{ V}$$

H_2SeO_4 oxidises concentrated hydrochloric acid, for example,

$$\overset{+6}{H_2Se}O_4 + 2HCl \rightleftharpoons \overset{+4}{H_2Se}O_3 + Cl_2 + H_2O$$

Because of the liberation of atomic chlorine, a mixture of H_2SeO_4 and HCl is a very strong oxidant that dissolves gold and platinum. The oxidising properties of H_6TeO_6 are weaker than those of H_2SeO_4.

Apart from their use in semiconductor technology, selenium and tellurium compounds are employed in the chemical synthesis, in particular, of various organo-selenium and organo-tellurium compounds. Many compounds of selenium and tellurium are very toxic. Polonium is even more dangerous because of its radioactivity.

CHAPTER 5

Group V *p* Elements

The elements of the main subgroup of Group V are nitrogen N, phosphorus P, arsenic As, antimony Sb, and bismuth Bi. In accordance with the electronic configuration of their atoms

N $1s^2 2s^2 2p^3$

P $2s^2 2p^6 3s^2 3p^3$

As $3s^2 3p^6 3d^{10} 4s^2 4p^3$

Sb $4s^2 4p^6 4d^{10} 5s^2 5p^3$

Bi $4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^3$

nitrogen and phosphorus are typical elements, while arsenic, antimony, and bismuth are grouped as the arsenic subgroup. The main

constants of the Group V *p* elements are as follows:

	$_{7}N$	$_{15}P$	$_{33}As$	$_{51}Sb$	$_{83}Bi$
Atomic mass	14.0067	30.9738	74.9216	121.75	208.980
Valence electrons	$2s^22p^3$	$3s^23p^3$	$4s^24p^3$	$5s^25p^3$	$6s^26p^3$
Metallic atom radius, nm	0.071	0.13	0.148	0.161	0.182
Covalent atom radius, nm	0.070	0.110	0.118	0.136	0.146
Conventional E^{3-} ion radius, nm	0.148	0.186	0.191	0.208	0.213
E^{5+} ion radius, nm	0.015	0.035	0.047	0.062	0.074
$E^{\circ} \rightarrow E^{+}$ ionisation energy, eV	14.53	10.49	9.82	8.64	7.29
Abundance, mole per cent	0.25	0.05	1.5×10^{-4}	5×10^{-6}	1.7×10^{-6}
Natural isotopes	^{14}N (99.64 %) ^{15}N (0.36 %)	^{31}P (100 %)	^{75}As (100 %)	^{121}Sb (57.3 %) ^{123}Sb (42.7 %)	^{209}Bi (100 %)

As will be seen from this table, the atoms and ions increase in size in the series As—Sb—Bi, which leads to a fall in their ionisation energies, a weakening of their nonmetallic character, and a strengthening of their metallic properties.

5.1. Nitrogen

Nitrogen ($1s^22s^22p^3$) is a typical nonmetal, in electronegativity (3.0) it is second only to fluorine and oxygen. Like the other *p* elements of the second period, it can have four valence orbitals in the sp^3, sp^2, or *sp* hybridisation state. In the last two states, one or two π bonds respectively may be formed. The oxidation numbers of nitrogen in its compounds are -3, -1, $+1$, $+3$ and $+5$ and also $+2$ and $+4$.

Natural nitrogen consists of two stable isotopes, ^{14}N (99.635 per cent) and ^{15}N (0.365 per cent). Its abundance is 0.03 mole per cent, the bulk of it (78 per cent by volume) being in the atmosphere in the form of the simple substance. The most important nitrogen minerals are Chile saltpetre $NaNO_3$ and Indian saltpetre KNO_3. Nitrogen is a constituent of proteins of all plant and animal organisms; it has been discovered in nebulae and in the solar atmosphere. It exists on Uranus and Neptune.

The simple substance. The electronic configuration of the nitrogen molecule N_2 is

$$[\sigma_s]^2 [\sigma_s^*]^2 [\pi_{x,y}]^4 [\sigma_z]^2$$

which corresponds to triple bonding between the atoms N≡N (d_{NN} = 0.1095 nm). Consequently the molecule is extraordinarily stable:

$$N_2 \rightleftharpoons 2N, \quad \Delta H^\circ_{298} = 945 \text{ kJ}, \quad K_{298} = 10^{-120}$$

Even at 3000 °C the degree of dissociation of molecular nitrogen is only 0.1 per cent.

Because of the stability of the N_2 molecule, many nitrogen compounds are endothermic. The entropy of their formation, moreover, is negative (N_2 being a gas). The chemical activity of molecular nitrogen is therefore very low, while nitrogen compounds are thermally unstable and decompose relatively easily when heated, which explains why nitrogen is present on Earth mainly in the free state.

The N_2 molecule is not highly polarised. The forces interacting between N_2 molecules are very weak and cannot prevent their chaotic motion (the enthalpy factor being much weaker than the entropy factor). In normal conditions molecular nitrogen is therefore a gas. The melting point of nitrogen is —210 °C and the boiling point —195.8 °C. It is barely soluble in water or other solvents.

In normal conditions nitrogen reacts directly only with lithium to form Li_3N. When nitrogen molecules are activated (by heating, electric discharge, ionising radiation) they usually act as oxidants, and only in the reaction with fluorine and oxygen are they reductants.

In industry nitrogen is produced by fractional distillation of liquid air. In the laboratory it is obtained by thermal decomposition of its compounds, usually NH_4NO_2:

$$\overset{-3}{N}H_4\overset{+3}{N}O_2 = \overset{0}{N_2} + 2H_2O$$

The bulk of the nitrogen obtained is used to synthesise ammonia. It is also used as an inert medium in the chemical and other industries.

Compounds of nitrogen (o.s. —3). At high temperatures, nitrogen oxidises many metals and nonmetals to form *nitrides*:

$$3Mg + N_2 = Mg_3N_2, \quad 2B + N_2 = 2BN, \quad 3H_2 + N_2 = 2H_3N$$

The properties of nitrides change more or less regularly in the periods and groups of the periodic system. A transition from basic to acidic nitrides, for example, is observed in the short periods:

$$\underbrace{Na_3N,\ Mg_3N_2}_{\text{Basic}} \qquad \underset{\text{Amphoteric}}{AlN} \qquad \underbrace{Si_3N_4,\ P_3N_5,\ S_4N_4,\ Cl_3N}_{\text{Acidic}}$$

The nitrides of Group I and II *s* elements (e.g. Li_3N and Mg_3N_2) are crystalline solids. Nitrides of this type are quite active chemically. They are easily decomposed, for example, by water to form alkali and ammonia

$$\underset{\text{Basic}}{Li_3N} + 3HOH = 3LiOH + H_3N$$

Halogen nitrides are endothermic compounds. Liquid Cl_3N has only been isolated in the free state ($\Delta H_f^\circ = 229$ kJ/mol). It easily decomposes explosively. By its chemical nature it is acidic

$$\underset{\text{Acidic}}{Cl_3N} + 3H_2O = 3HClO + H_3N$$

The nitrides BN and AlN, and Si_3N_4 and Ge_3N_4 are solid polymers with high melting points (2000 to 3000 °C). They are either dielectrics or semiconductors.

There are many nitrides of *d* elements. They are crystalline substances of varying composition, usually MN (TiN, VN, CrN) or M_2N (Nb_2N, Cr_2N, Mo_2N). They display metallic properties, such as metallic lustre and electron-type conductivity. The nitrides of this type are very hard and infusible (often exceeding the infusibility of the initial metal):

	Ti	Zr	Hf	V	Nb	Ta
M. p., °C	1668	1855	2220	1900	2470	3015
	TiN	**ZrN**	**HfN**	**VN**	**NbN**	**TaN**
M. p., °C	3220	2950	2982	2050	2573	3090
$\Delta G_{f,\,298}^\circ$, kJ/mol	−308	−336	−340	−224	−215	−218

Most nitrides of *d* elements are very stable chemically, are not decomposed by water, acid solutions, or molten metals, and are resistant to oxidation by air. These properties make them employable as high-strength materials.

Binary nitrides of *d* elements have also been obtained. Their composition corresponds to the characteristic oxidation states of the elements, e.g. Zr_3N_4 or Ta_3N_5.

The interaction between basic and acidic nitrides gives mixed nitrides, e.g. Li_3AlN_2, Li_5GeN_3, Li_5TiN_3, Li_9WN_5:

$$Li_3N + AlN = Li_3AlN_2$$

$$\underset{\text{Basic}}{5Li_3N} + \underset{\text{Acidic}}{Ge_3N_4} = 3Li_5GeN_3$$

The covalent nitride of most practical importance is hydrogen nitride H_3N or *ammonia*. In normal conditions it is a colourless gas with a sharp suffocating odour. The H_3N molecule has the configuration of a trigonal pyramid ($d_{NH} = 0.1015$ nm, $\angle HNH = 107.3°$). According to the valence bond theory, the nitrogen atom in the molecule is in the sp^3 hybridisation state. Three of its four sp^3 hybrid orbitals are involved in the formation of three N—H σ bonds, while the fourth orbital is occupied by a nonbonding electron pair. In terms of molecular orbital theory, this corresponds to the filling of three bonding and one almost nonbonding molecular σ orbital:

$$[\sigma_s]^2\,[\sigma_x]^2\,[\sigma_y]^2\,[\sigma_z^{non}]^2$$

The energy diagram of the molecular orbitals of ammonia is given in Fig. 152. Seven molecular orbitals (three σ, three σ* and one σ_z^{non}) arise from seven initial atomic orbitals (2*s*, $2p_x$, $2p_y$ and $2p_z$ nitrogen orbitals and 1*s* orbitals of the three hydrogen atoms).

In accordance with the orbital distribution of electrons, the H_3N molecule has three first ionisation potentials (22.4, 15.2 and 10.5 eV) which corresponds to the removal of an electron from one of the three occupied energy levels.

Because of sp^3 hybridisation of the valence orbitals of the nitrogen atom, the two-electron nonbonding cloud is positively oriented in space (see Fig. 50), so that the ammonia molecule is a very pronounced donor of an electron pair and has high polarity ($\mu = 0.49 \times 10^{-29}$ C·m).

The polarity of the N—H bond accounts for the hydrogen bond between the H_3N molecules. The melting point (—77.75 °C) and the boiling point (—33.42 °C) of ammonia are therefore quite high; it has a considerable enthalpy of evaporation and is readily liquefied; hence its use in refrigerators. Liquid ammonia is stored in steel cylinders.

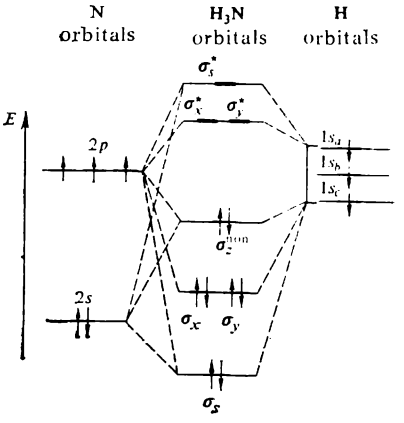
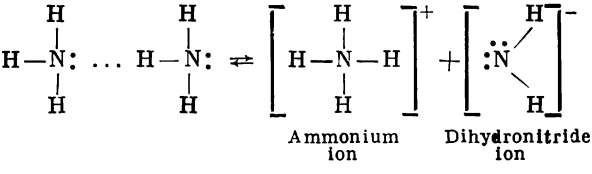


Fig. 152. Energy diagram of a pyramidal molecule (H_3N) without π bonding

Ammonia occupies a special position among the hydrogen compounds of Group V *p* elements, like that of water among the Group VI ones and hydrogen fluoride among the hydrogen halides.

The self-ionisation of ammonia is negligible



and its ionic product $[NH_4^+][NH_2^-]$ is only 2×10^{-33} (at —50 °C).

Liquid ammonia, like water, is a strong ionising solvent; the NH_4^+ derivatives in it (like the OH_3^+ derivatives in water) behave as acids (*ammono acids*) and the derivatives of NH_2^- (like derivatives of OH^- in water) as bases (*ammono bases*). For example, NH_4Cl and NH_4NO_3 are strong acids in liquid ammonia, while KNH_2 and $Ba(NH_2)_2$ are bases. The dihydronitrides $Zn(NH_2)_2$ and $Al(NH_2)_3$ behave like amphoteric compounds. The derivatives of NH_2^- are

also known as *amides* and the derivatives of the NH^{2-} radical as *imides*.

Several types of reaction in liquid ammonia and, for comparison, in water are given below.

1. A neutralisation reaction takes place between ammono acids and ammono bases

$$KNH_2 + NH_4Cl = KCl + 2H_3N$$
$$KOH + OH_3Cl = KCl + 2H_2O$$

2. Basic and amphoteric nitrides, hydronitrides, and dihydronitrides, that are insoluble in liquid ammonia, dissolve in ammono acids

$$Ca_3N_2 + 6NH_4Cl = 3CaCl_2 + 8H_3N$$
$$CaO + 2OH_3Cl = CaCl_2 + 3H_2O$$
$$Zn(NH_2)_2 + 2NH_4Cl = [Zn(NH_3)_4]Cl_2$$
$$Zn(OH)_2 + 2OH_3Cl = [Zn(OH_2)_4]Cl_2$$

3. Acidic and amphoteric nitrides, hydronitrides, and dihydronitrides, insoluble in liquid ammonia, dissolve in ammono alkalis

$$6KNH_2 + C_3N_4 = 3K_2[CN_2] + 4H_3N$$
$$2KOH + CO_2 = K_2[CO_3] + H_2O$$
$$2KNH_2 + Zn(NH_2)_2 = K_2[Zn(NH_2)_4]$$
$$2KOH + Zn(OH)_2 = K_2[Zn(OH)_4]$$

4. Substances dissolved in liquid ammonia are ammonolysed:

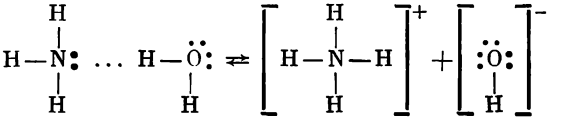
$$PCl_5 + 8H_3N = PN(NH_2)_2 + 5NH_4Cl$$
$$PCl_5 + 9H_2O = PO(OH)_3 + 5OH_3Cl$$
$$SO_2Cl_2 + 4H_3N = SO_2(NH_2)_2 + 2NH_4Cl$$
$$SO_2Cl_2 + 4H_2O = SO_2(OH)_2 + 2OH_3Cl$$

5. Simple substances react with liquid ammonia, ammono acids, and ammono alkalis

$$2K + 2H_3N = 2KNH_2 + H_2$$
$$2K + 2H_2O = 2KOH + H_2$$
$$Mg + 2NH_4Cl + 4H_3N = [Mg(NH_3)_6]Cl_2 + H_2$$
$$Mg + 2OH_3Cl + 4H_2O = [Mg(OH_2)_6]Cl_2 + H_2$$

Liquid ammonia is widely employed as a solvent in chemical synthesis.

Ammonia dissolves very readily in water (one volume of water dissolving about 700 volumes of H_3N at 20 °C). Its good solubility is due to the formation of a hydrogen bond between the molecules of H_3N and H_2O. Since the H_3N molecule is a better proton acceptor than H_2O (see p. 141), the solution is ionised as follows:



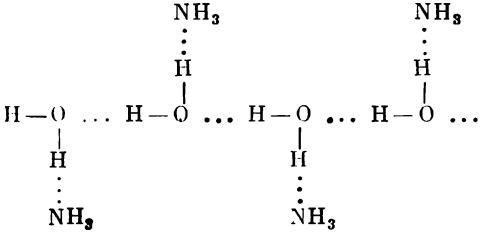
The appearance of the OH^- ions produces an alkaline medium but, as will be seen from the ionisation constant

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3 \cdot H_2O]} = 1.8 \times 10^{-5}$$

the reaction is insignificant. Only 0.4 per cent of the H_3N molecules enters the ionisation reaction in a 1 *M* solution.

In the interaction of the NH_4^+ and OH^- ions molecules of H_3N and H_2O are formed again (with a hydrogen bond between them). Consequently there is no ionic compound NH_4OH (ammonium hydroxide), just as oxonium hydroxide OH_3OH and ammonium dihydro nitride NH_4NH_2 also do not exist.

Two crystal hydrates, $H_3N \cdot H_2O$ (m.p. −79 °C) and $2H_3N \cdot H_2O$ (m.p. −78.8 °C) are precipitated from aqueous solutions of ammonia, but are stable only at low temperatures. The water and ammonia molecules are linked by a hydrogen bond in crystal hydrates; $H_3N \cdot H_2O$, for example, has a structure in which the water molecules form chains (through hydrogen bonds), which are linked by ammonia molecules in a trimeric lattice (also through hydrogen bonds):



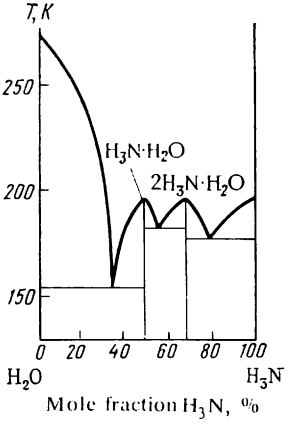


Fig. 153. Phase diagram of the H_2O—H_3N system

The NH_4^+ ion is formed much more easily by the interaction of ammonia with acids, for example

$$H_3N + HClO_4 = NH_4ClO_4$$

The stronger the acid, the more stable the ammonium derivative is; the thermal stability of the salts, for example, increases in the series NH_4F—NH_4Cl—NH_4Br—NH_4I.

Because of similarity of the ionic dimensions of NH_4^+ ($r_{NH_4^+}$ = 0.143 nm) and K^+ (r_{K^+} = 0.133 nm) the salts of ammonia are similar in properties to potassium salts. Almost all ammonia salts, for instance, are readily soluble in water and dissociate completely in it. A difference is seen in hydrolysis since the NH_4^+ and OH^- ions are bound into ammonia hydrate and form an acidic medium:

$$NH_4^+ + 2HOH \rightleftharpoons H_3N \ldots H_2O + OH_3^+, \quad K_{298} = 5.5 \times 10^{-19}$$

When heated, ammonia displays the reducing properties oxidising usually to elementary nitrogen:

$$\overset{-3}{4H_3N} + 3O_2 = \overset{0}{2N_2} + 6H_2O, \quad K_{298} = 10^{229}$$

This reaction is practically irreversible ($\Delta H < 0$). The reducing properties of H_3N are utilised in soldering to remove oxides from the metal surface with NH_4Cl (*sal ammoniac*).

Ammonia is produced industrially by synthesising the simple substances:

$$1/2N_2(g) + 3/2H_2(g) \rightleftarrows H_3N(g), \quad \Delta H^\circ_{298} = -46 \text{ kJ}$$
$$\Delta S^\circ_{298} = -103 \text{ J/K}$$

Since the enthalpy of formation of ammonia is low and its synthesis is accompanied with a fall in entropy in accordance with Le Chatelier's principle, the process is carried out (Fig. 154) at high pressures (10^7-10^8 Pa). Catalysts are used to accelerate the reaction.

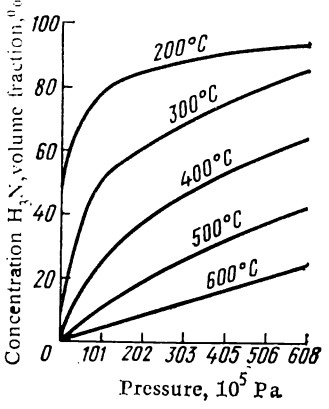


Fig. 154. Equilibrium concentration of ammonia in a nitrogen-hydrogen mixture ($N_2 + 3H_2$) as a function of pressure and temperature

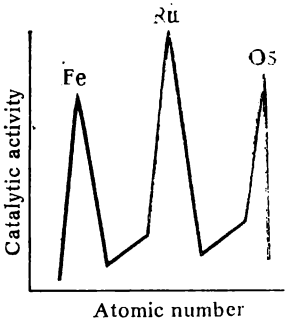


Fig. 155. Dependence of the catalytic activity of selected metals in the $2H_3N \rightleftarrows 3H_2 + N_2$ reaction (800 °C, 1×10^5 Pa) on atomic number

The simple substances of the iron subgroup elements (Fig. 155) are most effective catalysts in this process. An iron catalyst (plus activators) is usually employed in the industrial synthesis of ammonia, which is carried out at 400 to 500 °C.

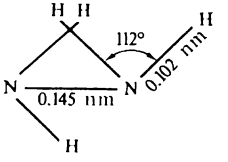
Ammonia is also liberated during the coking of coals. In the laboratory it is obtained by the action of alkalis on ammonium salts. Most of the ammonia produced is used to prepare nitric acid and nitrogeneous fertilizers (liquid ammonia and its aqueous solutions,

NH_4NO_3, $(NH_4)_2SO_4$, etc.). An aqueous solution of ammonia (*ammonia water*) is an important reagent for various reactions.

Compounds of nitrogen (o.s.— 2). Like oxygen, nitrogen forms peroxide compounds known as *pernitrides*, which can be regarded as derivatives of the radicals formed during consecutive disruption of bonds in the N_2 molecule:

	$\ddot{N}\equiv\ddot{N}$	$-\ddot{N}=\ddot{N}-$	$>\ddot{N}-\ddot{N}<$
d_{NN}, nm	0.1095	0.125	0.1455
k_{NN}, N/m	2360	—	250

The simplest pernitride is that of hydrogen, H_4N_2 (*hydrazine* or *diamide*). The hydrazine molecule is polar ($\mu = 0.62 \times 10^{-29}$ C·m). Its structure can be represented as follows:



It is a colourless liquid melting at 2 °C and boiling at 113.5 °C. Its molecules are connected by hydrogen bonds. The self-ionisation of liquid hydrazine

$$N_2H_4 \ldots N_2H_4 \rightleftarrows N_2H_5^+ + N_2H_3^-$$

$$H_4N_2 \ldots H_4N_2 \rightleftarrows \left[\begin{array}{c} H \\ | \\ H-N-\ddot{N}-H \\ | \quad | \\ H \quad H \end{array}\right]^+ + \left[\begin{array}{c} \ddot{N}\ddot{:} \\ | \quad | \\ H-\ddot{N} \quad \ddot{N}: \\ | \quad | \\ H \quad H \end{array}\right]^-$$

Hydrazonium ion — Hydrazide ion

is insignificant. The ionic product $[N_2H_5^+][N_2H_3^-]$ is 2×10^{-25} (at —33.4 °C).

Hydrazine is a good ionising solvent. It is miscible with water and alcohol in any proportion. Aqueous solutions form an alkaline medium:

$$H_4N_2 \ldots HOH \rightleftarrows N_2H_5^+ + OH^-, \quad K_{b1} = 9.3 \times 10^{-7}$$
$$N_2H_5^+ \ldots HOH \rightleftarrows N_2H_6^{2+} + OH^-, \quad K_{b2} = 8.5 \times 10^{-15}$$

Being a donor of two electron pairs, hydrazine reacts with acids to form two series of hydrazonium derivatives (salts), e.g. $[N_2H_5]Cl$, $[N_2H_6]Cl_2$, $[N_2H_6]SO_4$.

Solutions of hydrazine are prepared by carefully oxidising ammonia by a hypochlorite:

$$2\overset{-3}{H_3}N + NaClO = \overset{-2}{H_4}N_2 + NaCl + H_2O$$

Hydrazine is an endothermic compound ($\Delta H^\circ_{f,298} = +56$ kJ/mol, $\Delta G^\circ_{f,298} = +149$ kJ/mol). It and derivatives of the hydrazonium ion are much less stable than ammonia and ammonium derivatives. It is a strong reductant:

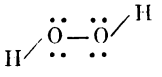
$$4KMnO_4 + 5\overset{-2}{H_4}\overset{}{N_2} + 6H_2SO_4 = 5\overset{0}{N_2} + 4MnSO_4 + 2K_2SO_4 + 16H_2O$$

When mixed with air, hydrazine burns, liberating much heat:

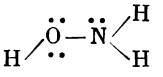
$$H_4N_2(l) + O_2(g) = N_2(g) + 2H_2O(l), \qquad \Delta H^\circ_{298} = -622 \text{ kJ}$$

Hydrogen pernitride H_2N_2 (*diimide*) is very unstable, but many organic derivatives of it are known.

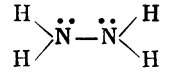
Compounds of nitrogen (o.s. −1). *Hydroxylamine* occupies an intermediate position between hydrogen peroxide and hydrogen pernitride (as regards its composition and structure):



Hydrogen peroxide



Hydroxylamine

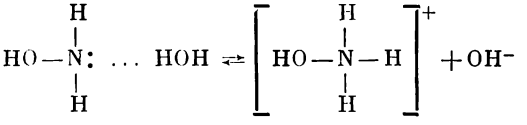


Hydrazine

It is a white crystalline solid melting at 33 °C ($\Delta G^\circ_f = -17$ kJ/mol), formed by the reduction of an HNO_3 solution by atomic hydrogen during electrolysis:

$$HNO_3 + 6H = NH_2OH + 2H_2O$$

Hydroxylamine is a donor of an electron pair and forms hydrogen bonds. It is miscible with water in any proportion. Like H_3N and H_4N_2, its aqueous solution is a weak base ($K_b = 8.9 \times 10^{-9}$):



Hydroxylammonium ion

It reacts with acids to yield salts of the hydroxylammonium ion $[NH_3OH]^+$, e.g. $[NH_3OH]Cl$, $[NH_3OH]NO_3$, $[NH_3OH]_2SO_4$

$$NH_2OH + HCl = [NH_3OH]Cl$$

Hydroxylammonium salts are stable, colourless, crystalline substances soluble in water.

Oxidising activity falls in the series H_2O_2—NH_2OH—H_4N_2 and reducing activity increases. Thus, while oxidising properties are most characteristic of H_2O_2, and reducing properties of H_4N_2, NH_2OH, though a strong reducing agent (in an alkaline medium)

also displays reducing properties in an acid medium:

$$\overset{-1}{2}NH_2OH + I_2 + 2KOH = \overset{0}{N_2} + 2KI + 4H_2O$$

Reductant

$$\overset{-1}{2}NH_2OH + 4FeSO_4 + 3H_2SO_4 = 2Fe_2(SO_4)_3 + (\overset{-3}{N}H_4)_2SO_4 + 2H_2O$$

Oxidant

Like hydrogen peroxide, NH_2OH decomposes readily (in particular when heated) on the disproportionation pattern:

$$\overset{-1}{3}NH_2OH = \overset{-3}{H_3N} + \overset{0}{N_2} + 3H_2O$$

Oxidant-reductant

Hydroxylamine and hydroxylammonium salts are used mainly in organic synthesis.

Being donors of electron pairs, NH_2OH and H_4N_2 (like H_3N) can be ligands in complex compounds, e.g. $[Co(NH_3)_6]Cl_3$, $[Co(NH_2OH)_6]Cl_3$, and $[Co(N_2H_4)_6]Cl_3$.

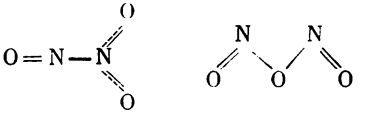
Compounds of nitrogen(III). The fluoride NF_3, oxide N_2O_3, oxyhalides NOHal, and fluorochloride NF_2Cl, and derivatives of the anion NO_2^-, are known for nitrogen with an oxidation state +3.

In normal conditions nitrogen *trifluoride* NF_3 is a colourless gas boiling at −129 °C and melting at −209 °C. It is prepared by oxidising ammonia with fluorine. The NF_3 molecule has a pyramidal structure (d_{NF} = 0.137 nm, ∠FNF = 102°). Unlike H_3N, the dipole moment of NF_3 (see Fig. 55) is very low, only 0.07×10^{-29} C·m. It has practically no electron-donating properties. Nitrogen trifluoride is quite stable to heat and various chemical actions, and reacts only at temperatures above 100 °C. It is practically insoluble in water and is only hydrolysed when an electric spark is passed through a mixture with water vapour.

The *oxide* of nitrogen(III) N_2O_3 can exist only in the solid state at low temperatures. As a liquid or vapour it dissociates considerably:

$$N_2O_3 \rightleftharpoons NO_2 + NO, \qquad \Delta G^\circ_{298} = -14 \text{ kJ}$$

It is obtained by cooling a mixture of NO_2 and NO. According to the findings of infra-red spectroscopy, its crystals consist of a stable $ONNO_2$ form and an unstable ONONO one:

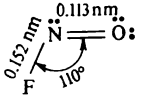


Liquid N_2O_3 is an intensely blue fluid freezing at −100 °C into pale blue crystals.

Nitrogen(III) oxide N_2O_3 is an acidic oxide that is easily absorbed by alkalis to form *nitrites*:

$$N_2O_3 + 2NaOH = 2NaNO_2 + H_2O$$

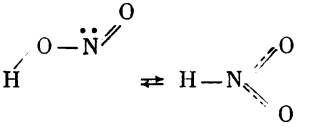
The molecules of nitrogen(III) *oxyhalides* (nitrosyl halides) are angular



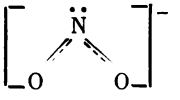
In normal conditions they are relatively unstable gases. The stability of compounds decreases in the series NOF—NOCl—NOBr, while NOI has not been obtained. The fluorides and oxyhalides, like nitrogen(III) oxide, are acidic compounds chemically, as is shown by their attitude to water:

$$2NF_3 + 3H_2O \text{ (vapour)} = N_2O_3 + 6HF, \qquad NOCl + H_2O = HNO_2 + HCl$$
$$N_2O_3 + H_2O = 2HNO_2$$

Hydrogen dioxynitrate(III) HNO_2 is known only in aqueous solution, which is the acid ($K_a = 4 \times 10^{-4}$) known as *nitrous acid*. Two tautomeric structures are known for HNO_2



The dioxynitrate(III), or the *nitrite ion* NO_2^- has an angular structure



The nitrites(III) of metals are quite stable, and those of the alkali metals are even sublimed without decomposition. The latter are obtained by dissolving N_2O_3 in alkalis.

Derivatives of nitrogen(III) have both reducing and oxidising properties:

$$2\overset{+3}{N}aNO_2 + 2KI + 2H_2SO_4 = I_2 + 2\overset{+2}{N}O + K_2SO_4 + Na_2SO_4 + 2H_2O$$
Oxidant

$$2KMnO_4 + 5\overset{+3}{N}aNO_2 + 3H_2SO_4 = 2MnSO_4 + 5\overset{+5}{N}aNO_3 + K_2SO_4 + 3H_2O$$
Reductant

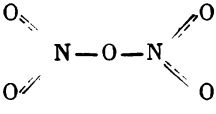
They are susceptible, moreover, to disproportionation:

$$3\overset{+3}{H}\overset{+3}{N}O_2 \rightleftharpoons \overset{+5}{H}\overset{+5}{N}O_3 + 2\overset{+2}{N}O + H_2O$$

Compounds of nitrogen(V). Nitrogen exhibits an oxidation state of +5 in its oxide N_2O_5, in oxynitride NON and dioxyfluoride NO_2F, and also in the trioxynitrate(V) ion NO_3^- and dinitride nitrate(V) ion NN_2^-. All these compounds can be regarded as derivatives of the tetravalent ion N^+:

Character of hybridisation of N^+	Configuration	Examples of compounds
sp^2 (2s, 2p)	triangular	$\overset{+5}{N}O_3^-$
sp	linear	$\overset{+5}{N}N_2^-$, $\overset{+5}{N}ON$

The *oxide* of nitrogen(V), N_2O_5, is a white crystalline substance (sublimes at 33 °C) formed by the NO_2^+ and NO_3^- ions. The structure of the gaseous N_2O_5 is probably as follows:

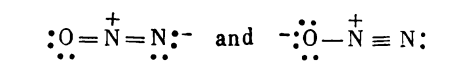


It is obtained by dehydrating HNO_3 (for example, with P_2O_5) or oxidising NO_2 by ozone. In ordinary conditions N_2O_5 (ΔG_f° = = +114 kJ/mol) decomposes gradually into NO_2 and O_2; it explodes when heated.

Nitrogen(V) *oxynitride* NON (nitrous oxide N_2O or *laughing gas*) is obtained by decomposing ammonium nitrate (at 250 °C):

$$NH_4NO_3 = N_2O + 2H_2O$$

It is a colourless gas (m.p., —91.0 °C, b.p., —88.5 °C) with a slight, pleasant odour. In accordance with *sp* hybridisation of N^+ valence orbitals, the molecule has a linear structure ($\mu = 0.05 \times \times 10^{-28}$ C·m, $d_{NN} = 0.113$ nm, $d_{NO} = 0.118$ nm) with the following interposition of the valence schemes:



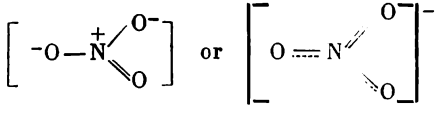
which corresponds to the following electron configuration (see Fig. 42):

$$[2s_a]^2[2s_b]^2[\sigma_s]^2[\sigma_z]^2[\pi_{x,y}]^4[\pi^{non}_{x,y}]^4$$

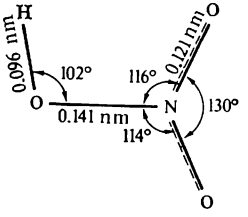
N_2O is decomposed as soon as slightly heated, liberating oxygen ($\Delta G^0_f = +104$ kJ/mol). For that reason carbonaceous substances can burn in it, its mixtures with hydrogen and ammonia are explosive. Nitrogen(V) oxynitride is soluble in water but does not form stable compounds.

Nitrogen(V) oxyfluoride NO_2F (nitronyl fluoride) is a colourless gas (m.p. —166 °C, b.p. —72 °C). It is a strong oxidant. Being an acidic compound, it is decomposed by water into HNO_3 and HF.

The *trioxynitrate*(V) ion NO_3^- has the shape of a planar triangle ($\angle ONO = 120°$, $d_{NO} = 0.122$ nm) because of sp^2 hybridisation of the valence orbitals of the nitrogen:



The molecule of hydrogen trioxynitrate(V) HNO_3 has the following structure



In ordinary conditions HNO_3 is a colourless liquid (density 1.52 g/cm³), boiling at 84.1 °C and solidifying into a transparent crystalline mass at —41.6 °C.

The self-ionisation of liquid HNO_3 is insignificant. It is miscible with water in any proportion; the solutions are the strong acid known as *nitric acid*. In the laboratory nitric acid is prepared by the action of concentrated sulphuric acid on sodium nitrate. In industry it is produced by a stepped process consisting of the oxidation of H_3N to NO by atmospheric oxygen over a platinum catalyst

$$4H_3N + 5O_2 = 4NO + 6H_2O, \quad K_{298} = 10^{163}$$

oxidation of NO to NO_2

$$2NO + O_2 = 2NO_2$$

and the latter's subsequent interaction with water

$$2NO_2 + H_2O = HNO_3 + HNO_2$$

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

Nitric acid has marked oxidising properties

$$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O, \quad E^\circ_{298} = 0.96 \text{ V}$$
$$NO_3^- + 2H^+ + 1e^- = NO_2 + H_2O, \quad E^\circ_{298} = 0.80 \text{ V}$$

It destroys animal and vegetable tissues, and oxidises almost all metals and nonmetals. Which reaction product will be formed depends on its concentration temperature and the activity of the simple substance. Figure 156 shows the effect of the concentration of HNO_3 on the character of its reduction products in reactions with iron. Quite dilute nitric acid is mainly reduced to NH_4NO_3; as the concentration increases, NO is more likely to be formed; concentrated HNO_3 is reduced to NO_2.

A mixture of HNO_3 with three parts of HCl is known as *aqua regia*. It dissolves platinum, gold, and other noble metals, converting them into complex chlorides (see p. 614). In a neutral medium the nitrate ion NO_3^- does not display hardly any oxidising properties

$$NO_3^- + H_2O + e^- = NO_2 + 2OH^-,$$
$$E^\circ_{298} = -0.88 \text{ V}$$

but it is an effective oxidant when melted:

$$Cr_2O_3 + 6NaNO_3 + 4KOH = 2K_2CrO_4 + 6NaNO_2 + 2H_2O$$

Hydrogen trioxynitrate(V) decomposes easily when heated or exposed to light:

$$4HNO_3 = 4NO_2 + O_2 + 2H_2O$$

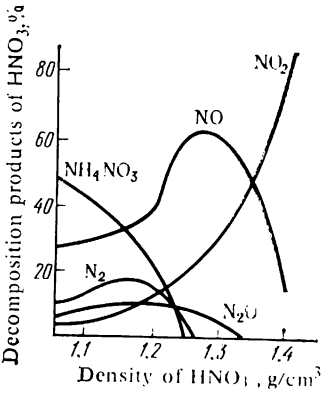


Fig. 156. Effect of HNO_3 concentration on the character of the products of its reduction by iron

The nitrates of most other elements are stable. Those of metals are soluble in water.

Nitrates are of great practical significance. They are used as fertilizers (especially potassium and ammonium nitrates). Nitric acid is used to make artificial fertilizers, explosives, organic dyestuffs, plastics, and many other products.

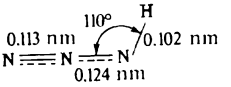
The *dinitride nitrate*(V) or *azide* ion, NN_2^- (N_3^-), has a linear structure ($d_{NN} = 0.115$ nm) in accordance with *sp* hybridisation of valence N^+ orbitals:

$$\left[{}^{-}\!:\!\ddot{N}=\overset{+}{N}=\ddot{N}\!:^{-} \right]^-$$

The distribution of valence electrons in its molecular orbitals corresponds to the following electron configuration (see Fig. 42):

$$[2s_a]^2[2s_b]^2[\sigma_s]^2[\sigma_z]^2[\pi_{x,\,y}]^4[\pi^{non}_{x,\,y}]_4$$

The structure of the hydrogen dinitride nitrate(V) HNN_2 (HN_3) is given below



In normal conditions HNN_2 is a colourless, volatile liquid (m.p. −80 °C, b.p. 37 °C) with a pungent odour. It and certain other azides explode when struck or heated; because of this property lead azide $Pb(N_3)_2$ is used as a detonator. Ionic azides, on the contrary, are relatively stable, and decompose without explosion when heated to 300 °C:

$$2NaNN_2(s) = 2Na(l) + 3N_2(g)$$

This reaction is employed to obtain nitrogen of high purity. The aqueous solution of HNN_2 is *hydrazoic* (*hydronitric*) *acid* ($K_a = 2.0 \times 10^{-5}$), which is comparable in strength with acetic acid. Dilute solutions of HNN_2 are more or less stable. The acid is prepared by the interaction of hydrazine and nitrous acid:

$$H_4N_2 + HNO_2 = HNN_2 + 2H_2O$$

The initial materials for obtaining other azides is $NaNN_2$, which is obtained by the action of N_2O on $NaNH_2$ at 200 °C:

$$NaNH_2 + O{=}\overset{+}{N}{=}N^- \rightarrow NaNN_2 + H_2O$$

The NN_2^- ion is an oxidant; HNN_2 resembles HNO_3 in oxidising properties while HNO_3, for instance, reacts with metals to yield the oxide of nitrogen(II) and water, HNN_2 forms nitrogen(III) nitride N_2 and H_3N:

$$Cu + 3\overset{+5}{H}NN_2 = Cu(NN_2)_2 + \overset{0}{N_2} + H_3N$$

$$3Cu + 8\overset{+5}{H}NO_3 = 3Cu(NO_3)_2 + 2\overset{+2}{N}O + 4H_2O$$

A mixture of HN_3 and HCl behaves like aqua regia.

A pentafluoride of nitrogen with oxidation state +5 has not been obtained. It is supposed that this compound does not exist because five fluorine atoms can hardly be stably coordinated around a small nitrogen atom. Numerous salts of the *fluoroammonium* ion NF_4^+, however, have recently been synthesised: $[NF_4]BF_4$, $[NF_4]EF_6$ (where E = P, As, Sb, Bi), $[NF_4]_2EF_6$ (E = Ti, Ge, Ni, etc.). These salts are quite stable; $[NF_4]AsF_6$, for example, only begins to decompose at temperatures above 250 °C. Salts of the NF_4^+ ion are strong oxidants. Salts of the ions $NH_2F_2^+$ and NH_3F^+ have also been obtained. Like NH_4^+, the NF_4^+, $NH_2F_2^+$, NH_3F^+ ions are tetrahedral.

Compounds of nitrogen(I), nitrogen(II) and nitrogen(IV). Like chlorine, quite stable oxides with an odd number of electrons (NO

and NO_2) are characteristic of nitrogen. They can be regarded as stable free radicals. Both are endothermic compounds, their standard enthalpies ΔH_f° and Gibbs' energies of formation ΔG_f° being positive.

In ordinary conditions, nitrogen(II) *oxide* NO is a colourless gas (m.p., −163.7 °C, b.p., −151.7 °C). It is prepared in the laboratory by the action of dilute HNO_3 on copper; in industry it is produced by oxidising H_3N over a platinum catalyst. Unlike all the other oxides of nitrogen, NO can also be obtained by direct interaction of the simple substances:

$$1/2N_2(g) + 1/2O_2(g) = NO(g),$$

$$\Delta H_{298}^\circ = +90 \text{ kJ}$$

$$\Delta S_{298}^\circ = 9 \text{ J/K}, \quad K_{298} = 5 \times 10^{-31}$$

The synthesis of NO from the simple substances is accompanied with a rise in the system's entropy. Therefore, in accordance with the equation

$$\Delta G = \Delta H - T\,\Delta S$$

ΔG can become a negative value at the appropriate temperature (Fig. 157). The entropy factor then predominates. Since the ΔS of the process is insignificant, the negative value of ΔG_T is attained at high temperatures (of the order of 3000 °C); for all other oxides of nitrogen, ΔG is positive at all temperatures (see Fig. 157) because the ΔS of the formation of compounds from simple substances is negative. Other nitrogen oxides therefore cannot be synthesised directly.

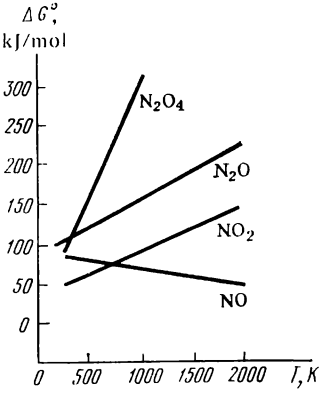


Fig. 157. Dependence of the standard Gibbs' energy of formation of nitrogen oxides on temperature

The activation energy of the synthesis of NO is high. It is formed by a chain reaction

$$O_2 + h\nu \rightarrow \cdot O\cdot + \cdot O\cdot$$

$$+$$

$$N_2 \rightarrow NO + \cdot N\cdot$$

$$+$$

$$O_2 \rightarrow NO + \cdot O\cdot, \text{ etc.}$$

The NO molecule is paramagnetic. According to the molecular orbital theory, one electron in NO is in the π_x^* orbital (see Table 38)

$$[\sigma_s]^2[\sigma_s^*]^2[\pi_{x,\,y}]^1[\sigma_z]^2[\pi_x^*]^1$$

i.e. the bond order in NO is 2.5. Its structural formula can be represented as :N $\overset{\cdot\cdot\cdot}{=}$ O:*.

* The three dots represent the bond formed by a pair of bonding electrons and the antibonding electron, which corresponds to a bond order of 0.5.

Table 38. **Molecular Orbital Distribution of Electrons and Properties of N_2 and NO Molecules and NO^+ and NO^- Molecular Ions**

Molecular orbitals	NO^+ $[N \equiv O]^+$	N_2 $[N \equiv N]$	NO $[N \overset{\cdot\cdot}{=} O]$	NO^- $[N \underset{\cdot\cdot}{\overset{\cdot\cdot}{=}} O]^-$
σ_z^*				
π_x^*, π_y^*				
σ_z				
π_x, π_y				
σ_s^*				
σ_s				
Bond order	3	3	2.5	2
Bond length, nm	0.106	0.11	0.115	0.118
Dissociation energy, kJ/mol	1046	941	678	—
Force constant k, N/m	2000	2240	1550	1200

This structure agrees well with the dipole moment ($0.02 \times \times 10^{-29}$ C·m) and with the bond length and force constant of the bond, which are intermediate between those of double and triple bonds:

$[N \underset{\cdot\cdot}{\overset{\cdot\cdot}{=}} O]^-$	$N \overset{\cdot\cdot}{=} O$	$[N \equiv O]^+$
$d_{NO} = 0.118$ nm	$d_{NO} = 0.114$ nm	$d_{NO} = 0.106$ nm
$k = 1200$ N/m	$k = 1550$ N/m	$k = 2000$ N/m

Because of its heightened multiplicity, the NO molecule is quite stable and only decomposes noticeably at 500 °C. Nitrogen(II) oxide is chemically active, is easily reduced in solution (by the action of SO_2 or Cr^{2+}) to NH_2OH and H_3N, and forms an explosive mixture with hydrogen. It is easily oxidised by oxygen, the halogens, etc.:

$$2NO + O_2 = 2NO_2, \qquad \Delta G^\circ_{298} = -70 \text{ kJ}$$
$$2NO + Cl_2 = 2NOCl, \qquad \Delta G^\circ_{298} = -39 \text{ kJ}$$

The unpaired electron in the NO molecule is in a disadvantageous, low energy, antibonding π^* molecular orbital and therefore cannot form stable bonds, which explains the absence of a tendency for NO to dimerise into N_2O_2. Only at low temperatures can NO dimerise into solid nitrogen(II) oxide (blue), which consists of unstable diamagnetic N_2O_2 molecules.

Nitrogen(II) oxide, however, reacts with other free radicals and so is used as an inhibitor of chain reactions. When a reaction proceeds according to a radical-chain mechanism, the addition of NO leads to a termination of the chain and to a sudden slowing down of the reaction.

The ionisation energy of NO is 9.27 eV, that is to say, it is much lower than that of N_2 (15.58 eV) and O_2 (12.08 eV). Its molecule can lose its unpaired electron from the π^* molecular orbital to form the NO^+ *nitrosyl* (*nitrosonium*) ion:

$$:N \vdots\vdots O: - e^- \rightarrow [:N \equiv O:]^+$$

The NO^+ ion is isoelectronic with the N_2 molecule. Unlike NO it is diamagnetic. Its structure corresponds to the electron configuration shown in Table 38:

$$[\sigma_s]^2 [\sigma_s^*]^2 [\pi_{x,y}]^4 [\sigma_z]^2$$

Derivatives of the NO^+ ion are, for example, $[NO]ClO_4$ and $[NO]_2SeO_4$, which are salt-like substances with a melting point of the order of 70 to 200 °C, easily decomposed by water. They can be obtained by the interaction of N_2O_3 and concentrated acids, for example,

$$N_2O_3 + H_2SeO_4 = [NO]_2SeO_4 + H_2O$$

In reactions with more active metals in liquid ammonia NO acts as an oxidant;

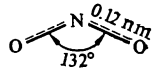
$$Na + NO = Na^+NO^-$$

$$:N \vdots\vdots O: + e^- \rightarrow [:N \vdots\vdots O:]^-$$

The derivatives of NO^- are unstable and have not been sufficiently studied.

The NO molecule acts as a ligand in the various complexes known as *nitrosyl complexes*. NO belongs in character to ligands of the σ and π donor and π acceptor type.

Nitrogen *dioxide* NO_2 is a brown toxic gas (m.p., −11.2 °C, b.p., 21 °C). Its molecule is paramagnetic and has an angular shape:



The bond length d_{NO} (0.120 nm) is intermediate between that of the simple (0.143 nm) and double (0.118 nm) bonds, which corresponds to a bond order of 1.5.

Taking the NO_2 molecule as an example, let us consider the structure of triatomic molecules with angular shape and π bonds in more detail. In the formation of the NO_2 molecule, $2s$, $2p_x$, $2p_y$ and $2p_z$ atomic orbitals of nitrogen and the $2p_x$, $2p_y$ and $2p_z$ orbitals of two oxygen atoms are involved. Ten molecular orbitals are formed from the ten atomic orbitals. Since the NO_2 and H_2O molecules have an angular shape, the σ orbitals of NO_2 are similar to the σ orbitals of the H_2O molecule (see Fig. 146). These five molecular orbitals: σ_s and $\sigma^*_{s(z)}$,

σ_z and σ_z^*, and also σ_x^{non}. In contrast to H_2O, three-centre π_y and π_y^* molecular orbitals are formed in the NO_2 molecule by the $2p_y$ orbitals of nitrogen and $2p_y$ orbitals of the two oxygen atoms. Three orbitals of the oxygen atoms act, in

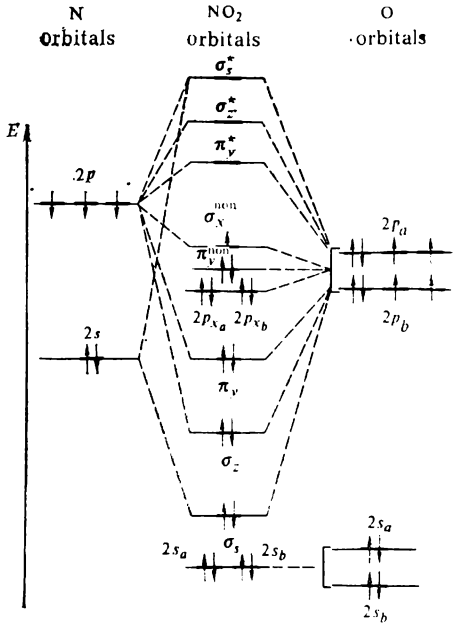


Fig. 158. Energy diagram of the NO_2 molecule

addition, as nonbonding molecular orbitals, which can be designated as π_y^{non}, $2p_{x_a}$ and $2p_{x_b}$. The energy diagram of the orbitals of the NO_2 molecule is shown in Fig. 158.

The seventeen valence electrons of the NO_2 molecule form the following configuration:

$$[2s_a]^2[2s_b]^2[\sigma_s]^2[\sigma_z]^2[\pi_y]^2[2p_{x_a}]^2[2p_{x_b}]^2[\pi_y^{non}]^2[\sigma_x^{non}]^1$$

The total number of bonding electrons is six: $(\sigma_s)^2\ (\sigma_z)^2\ (\pi_y)^2$ which corresponds to an average bond order of 1.5. The other electrons play a nonbonding role. In terms of valence bond theory, the nitrogen atom in NO_2 can be described by sp^2 hybridisation of valence orbitals (which arises from $2s$, $2p_x$ and $2p_z$ orbitals). One of the sp^2 hybrid orbitals (σ_x orbital) is occupied by an unpaired electron while the other two sp^2 orbitals are involved in the formation of two N—O σ bonds (two molecular σ_s and σ_z orbitals). The $2p_y$ orbitals of the nitrogen and two oxygens are involved in the formation of a delocalised π bond (molecular π_y orbital). The structure of the molecules of Cl_2O, O_3, SO_2, OF_2, ClO_2, NO_2^-, etc., is explained in a similar way. The NO_2^- ion, for example, has the following electron configuration

$$[2s_a]^2[2s_b]^2[\sigma_s]^2[\sigma_z]^2[\pi_y]^2[2p_{x_a}]^2[2p_{x_b}]^2[\pi_y^{non}]^2[\sigma_x^{non}]^2$$

When the NO_2 molecule loses a σ_x electron, it is converted into the nitrosyl ion NO_2^+, which has the linear structure

$$[O=N=O]^+$$

with an internuclear distance of $d_{NO} = 0.115$ nm. The nitrosyl ion is isoelectronic with the linear molecules of the CO_2 type (Fig. 42):

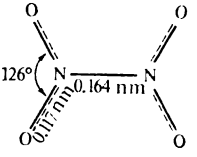
$$(2s_a)^2\,(2s_b)^2\,(\sigma_s)^2\,(\sigma_z)^2\,(\pi_x)^2\,(\pi_y)^2\,(\pi^{non}_x)^2\,(\pi^{non}_y)^2$$

Even in pairs, the NO_2 molecules are partly dimerised:

$$2NO_2 \underset{+150\ ^\circ C}{\overset{-11\ ^\circ C}{\rightleftharpoons}} N_2O_4, \quad \Delta H^\circ_{298} = -55.4\ kJ$$

Brown, paramagnetic — Colourless, diamagnetic

Both liquid and solid nitrogen dioxide are colourless, consisting of flat N_2O_4 molecules:



The NO_2 molecule can lose electrons (ionisation energy 9.78 eV) or gain them (electron affinity 1.62 eV):

$$NO_2 - e^- \rightarrow NO_2^+ \ (\textit{nitronium}\ \text{ion})$$
$$NO_2 + e^- \rightarrow NO_2^- \ (\textit{nitrite}\ \text{ion})$$

These transformations determine its ability to undergo disproportionation with water and alkali solutions

$$\overset{e^-}{\underset{\downarrow}{\ulcorner\!\!\urcorner}}$$
$$NO_2 + NO_2 + HOH \rightleftharpoons NO_2OH + HNO_2$$
$$2NO_2 + 2OH^- = NO_3^- + NO_2^- + H_2O$$

The nitronium ion NO_2^+ is formed during self-ionisation of liquid HNO_3

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$$

Derivatives of the *nitronium* ion NO_2^+ worth mentioning are $[NO_2]ClO_4$ and the solid nitrogen(V) oxide $[NO_2]NO_3$. Nitronium salts are crystalline substances that are chemically very active and rapidly hydrolysed by humid air. Nitronium salts can be prepared, for example, by the following reaction

$$N_2O_5 + HClO_4 = NO_2ClO_4 + HNO_3$$

Nitrogen dioxide is chemically active, and carbon, sulphur, and phosphorus burn in its atmosphere. It is produced in the laboratory by reacting copper with concentrated nitric acid

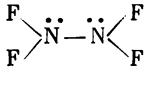
$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

or by thermal decomposition of certain oxynitrates(V):

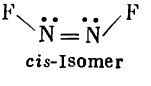
$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

Nitrogen dioxide is used as a nitrating agent, in particular, to prepare anhydrous nitrates.

Covalent compounds of atomic groupings N_2^{4+} and N_2^{2+} of the type of N_2F_4 and N_2F_2 can be regarded as derivatives of N(I) and N(II):

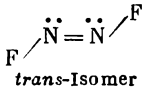


Tetrafluorohydrazine



cis-Isomer

or



trans-Isomer

Difluorodiazine

There are many salts in which the N_2F^+ and $N_2F_3^+$ ions act as cations, for example, $[N_2F]PF_6$, $[N_2F]AsF_6$, $[N_2F]SbF_6$ and $[N_2F_3]AsF_6$, and $[N_2F_3]SbF_6$. These salts are formed by the interaction of difluorodiazine N_2F_2 and tetrafluorohydrazine N_2F_4 with strong acceptors of fluoride ions, for example:

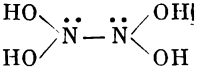
$$N_2F_2 + AsF_5 = [N_2F]AsF_6$$

$$N_2F_4 + AsF_5 = [N_2F_3]AsF_6$$

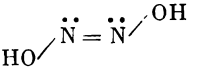
The conversion of the N_2F_2 and N_2F_4 molecules into the N_2F^+ and $N_2F_3^+$ cations respectively is accompanied with increasing N—N bond order, decreasing bond length, and increasing strength. Thus, in contrast to the N_2F_2 molecule ($d_{NN} = 0.121$ nm), the N—N bond in the N_2F^+ ion is triple ($d_{NN} = 0.101$ nm): $[N{\equiv}N{-}F]^+$. Thus the changes are the same as in the transformation of O_2 into O_2^+ through the removal of an electron from the outer antibonding orbital (see Table 34).

Salts of the N_2F^+ and $N_2F_3^+$ cations are very reactive, decomposing vigorously in contact with water, and are strong oxidants.

Of the covalent compounds formed by the radicals N_2^{4+} and N_2^{2+} the unstable hydroxides $N_2(OH)_4$ and $N_2(OH)_2$ are known also



Nitroxylic acid



Hyponirtous acid

5.2. Phosphorus

Phosphorus P ($1s^22s^22p^63s^23p^3$) is an analogue of nitrogen as regards number of valence electrons but, being an element of the third period, it differs substantially from it (nitrogen being an element of the second period): the phosphorus atom is larger, its ionisation energy lower, and its electron affinity and polarisability higher than those of nitrogen. Its maximum coordination number is six. As with other elements of the third period, πp—πp bonding is not characteristic of

the phosphorus atom so that, in contrast to nitrogen, the *sp* and sp^2 hybridisation states of phosphorus orbitals are unstable. The oxidation states of phosphorus range in its compounds from −3 to +5. The most characteristic one is +5.

From another point of view, the different properties of phosphorus and nitrogen are explained by the presence of 3*d* valence orbitals in the phosphorus atom.

Phosphorus forms its strongest bonds with fluorine and oxygen (Table 39).

Table 39. **Bond Energy of Compounds of P(III) and N(III)**

Bond	Energy, kJ/mol	Bond	Energy, kJ/mol	Bond	Energy, kJ/mol
PH	322	PF	489	NCl	123
NH	389	NF	272	PO	380
PC	272	PCl	318	NO	222
NC	334				

In accordance with its stable oxidation state, phosphorus is contained in the crust mainly in the form of phosphates(V). Its most common minerals are *phosphorite* $Ca_3(PO_4)_2$, *hydroxyapatite* $Ca_5(PO_4)_3(OH)$, and *fluorapatite* $Ca_5(PO_4)_3F$. Phosphorus is a constituent of animal organisms: hydroxyapatite forms the mineral part of bones, the teeth contain fluorapatite while there are complex organic derivatives of phosphorus in the cells of the brain and nerves.

The abundance of phosphorus in the crust is 0.05 mole per cent. It has only one natural isotope, ^{31}P, but radioactive isotopes of phosphorus have been obtained artificially.

The simple substances. Phosphorus atoms unite into diatomic P_2, tetratomic P_4. and polymeric $P_{2\infty}$ molecules. The P_2 molecules (d_{PP} = 0.19 nm) have a structure similar to that of nitrogen N_2; they exist at temperatures above 1000 °C.

In the liquid or dissolved state, or as a vapour (below 1000 °C) P_4 tetratomic molecules (tetrahedral configuration) are stable (see Table 27). As the vapour condenses, *white phosphorus* is formed (density, 1.8 g/cm^3), which has a molecular crystal lattice with P_4 molecules at the lattice points. White phosphorus is a soft, colourless, wax-like substance with a low melting point (m.p. 44.1 °C, b.p 275 °C), is volatile. and soluble in carbon disulphide and certain organic solvents. *It is extremely poisonous.*

The P—P bonds (d_{PP} = 0.221 nm, E_{P-P} = 200 kJ/mol) of the P_4 molecule are quite easily broken, which explains the high chemical activity of white phosphorus and its tendency to change into

more stable polymeric modifications (in particular when heated); e.g.

$$\text{P (white)} \rightarrow \text{P (red)}, \qquad \Delta H^\circ_{298} = -18 \text{ kJ}$$

In normal conditions, *black phosphorus* is the most stable form, but, because of its high activation energy, the other forms are not converted into it in normal conditions. It can be obtained from white phosphorus at 200 °C and 1.2×10^{10} Pa:

$$\text{P (white)} \rightarrow \text{P (black)}$$
$$\Delta H^\circ_{298} = -39 \text{ kJ}$$

Black phosphorus has an atomic layer lattice (Fig. 159) with a typical pyramidal arrangement of bonds. (The distance between neighbouring atoms is 0.218 nm and between layers, 0.368 nm; $\angle$PPP =

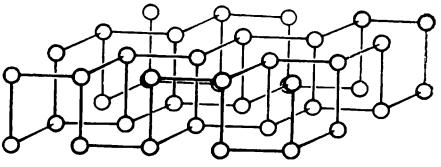


Fig. 159. **Structure of black phosphorus**

= 99°.) Outwardly black phosphorus (density, 2.7 g/cm³) looks like graphite, but it is a semiconductor (ΔE = 0.133 eV).

There are several forms of *red phosphorus*. Their structures have not been established with certainty, but they are known to be polymers consisting of pyramid-bonded atoms. The properties of red phosphorus vary, depending on how it is obtained; its density, for example, varies within limits of 2.0 to 2.4 g/cm³, its melting point between 585 °C and 600 °C, and its colour from dark brown to red and violet.

To liquefy or to dissolve red phosphorus, it is necessary to break the bonds in the polymer molecules. The polymer forms therefore have high melting points and are practically insoluble in any solvent. When red phosphorus sublimes (423 °C), its P_2 molecules are converted into a vapour and then recombine into P_4 molecules. Thus, the white form (and not the red) is formed when the vapour is condensed.

Red, and especially black, phosphorus is much more stable than the white. Thus, while white phosphorus ignites spontaneously in the air at temperatures as low as 50 °C, red phosphorus ignites only at temperatures above 250 °C and black phosphorus only at temperatures over 400 °C. Unlike white phosphorus, the high-polymer modifications of phosphorus are not poisonous. Because of its high chemical activity, white phosphorus should be stored under water and in the dark.

Phosphorus displays both reducing and oxidising properties. It is readily oxidised by oxygen, the halogens, sulphur, etc. In the absence of an oxidant, phosphorus(III) compounds are usually formed (P_2O_3, $PHal_3$, and P_2S_3), but with an excess of oxidant, phosphorus(V) compounds are formed (e.g. P_2O_5, $PHal_5$, and P_2S_5). The oxidising activity of phosphorus is seen during its reaction with metals. When heated in water, and especially in alkali solutions, phosphorus undergoes disproportionation.

Phosphorus is prepared industrially by heating calcium phosphate with carbon and sand in electric furnaces at a temperature of 1500 °C:

$$2\overset{+5}{Ca_3}(\overset{}{PO_4})_2\ (c) + 10\overset{0}{C}\ (c) + 6SiO_2\ (s) = 6CaSiO_3\ (s) + 10\overset{+2}{CO}\ (g) + \overset{0}{P_4}\ (g)$$

This reaction is endothermic but is accompanied with an increase in entropy. The temperature at which it proceeds is determined by the condition $T\Delta S > \Delta H$. The vapour evolving is condensed into white phosphorus, which is then converted into red phosphorus by prolonged heating at 280 °C to 340 °C. The bulk of the red form is used in the manufacture of matches.

Compounds of phosphorus (o.s. —3). When phosphorus is heated, it oxidises almost all metals to form *phosphides*. The proportion of any particular bond varies within wide limits in phosphides depending on the nature of the metal. Phosphides of Group II *s* elements with an E_3P_2 composition, for instance, can be regarded as ionic-covalent compounds; they are salt-like substances readily decomposed by water

$$Mg_3P_2 + 6H_2O = 3Mg(OH)_2 + 2H_3P$$

The phosphides of *d* elements (as a rule of the MP, MP_2 and M_3P type) are grey or black substances with a metallic lustre, conducting electricity. Their chemical activity is low.

Hydrogen phosphide H_3P (*phosphine*) is a covalent phosphide. Phosphorus hardly reacts with hydrogen, so phosphine (ΔG_f° = = +13.4 kJ /mol) is prepared indirectly, being obtained by hydrolysis of certain phosphides and by disproportionation of phosphorus heated in an alkaline medium:

$$2\overset{0}{P_4} + 3Ba(OH)_2 + 6H_2O = 3Ba(\overset{+1}{P}O_2H_2)_2 + 2\overset{-3}{H_3P}$$

The H_3P molecule (like H_3N) is a trigonal pyramid (d_{PH} = 0.142 nm, $\angle HPH$ = 93.5°), but its dipole moment is much lower ($0.18 \times \times 10^{-29}$ C·m). No hydrogen bond arises between the H_3P molecules, so that the melting and boiling points of phosphine (—133.8 °C and —87.42 °C respectively) are lower than those of ammonia. Phosphine is an *extremely poisonous* gas with an unpleasant odour.

The conversion of the pyramidal molecule H_3P into the tetrahedral PH_4^+ ion should be accompanied with a substantial change in the

bond angle ∠HPH (from 93.7 to 109.5°). Its electron-donating properties are therefore much weaker than those of H_3N; thus phosphine dissolves in water but does not form any compounds in doing so.

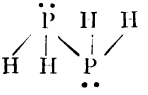
Phosphine's electron-donating properties are displayed only when stronger donors of protons ($HClO_4$ or HI) act on it, for example during the mixing of gaseous H_3P and HI:

$$H_3P(g) + HI(g) = PH_4I(c)$$

Unstable, colourless, crystalline derivatives of the *phosphonium* ion PH_4^+ are formed in this process. They are easily decomposed by water.

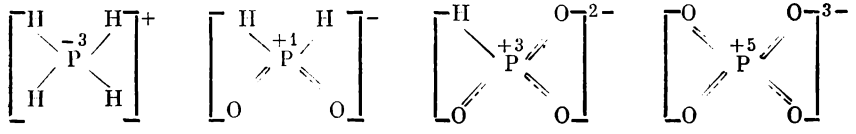
Phosphine and phosphonium derivatives are strong reductants; phosphine inflames spontaneously in air at 150 °C.

Hydrogen perphosphide H_4P_2 (*diphosphine*) is an analogue of hydrazine:



Diphosphine is a colourless liquid (m.p., −99 °C, b.p., 65.2 °C). It is formed together with H_3P during the hydrolysis of phosphides. It is a strong reductant, and inflames spontaneously in air.

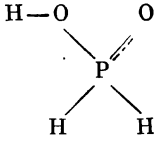
Compounds of phosphorus(I). Complexes in which oxygen atoms in addition to hydrogen atoms act as ligands are more stable than PH_4^+. Because of the π bonding the oxygen atoms stabilise the sp^3 hybridisation of phosphorus



Phosphonium ion Hypophosphite ion Phosphite ion Phosphate ion

All these ions have a tetrahedral or distorted tetrahedral structure. Allowing for the difference in the atoms' electronegativity, it can be taken that the oxidation state of phosphorus varies in this series from −3 to +5.

Derivatives of the $[PO_2H_2]^-$ complex (*hypophosphite ion*) can be regarded as compounds of phosphorus(I). The hydrogen derivative of this ion $H[PO_2H_2]$



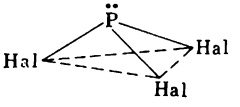
is a colourless crystalline solid in normal conditions (m.p., 26.5 °C). It dissolves readily in water to form a strong monobasic acid $H[PO_2H_2]$ known as *hypophosphorous* acid ($K = 7.9 \times 10^{-2}$). Its salts, *hypophosphites*, are readily soluble in water. The acid itself, and its salts, are strong reductants, which are oxidised to oxyphosphates(V). Hypophosphites are used as reducing agents in, for example, chemical nickel plating:

$$Ni^{2+} + \overset{+1}{[PO_2H_2]^-} + 2H_2O = \overset{0}{Ni} + \overset{+5}{PO_4^{3-}} + 4H^+ + \overset{0}{H_2}$$

Phosphorus(I) compounds exhibit hardly any oxidising properties, but undergo disproportionation when heated:

$$3H\overset{+1}{[PO_2H_2]} = \overset{-3}{H_3P} + 2H_2\overset{+3}{[PO_3H]}$$

Compounds of phosphorus(III). Three or four sp^3 hybrid orbitals of the phosphorus atom are involved in the formation of bonds in derivatives of P(III), which corresponds to a pyramidal or tetrahedral arrangement of the bonds. The structure of phosphorus *trihalide* $PHal_3$ molecules (like H_3P) thus has the configuration of a trigonal pyramid with the phosphorus atom at the apex (d_{PHal} = = 0.155 to 0.255 nm, ∠HalPHal is about 100°):

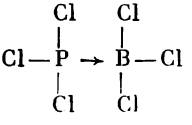


The polarity of the molecules decreases in the series PF_3—PCl_3—PBr_3—PI_3. Phosphorus trihalides have molecular lattices. In normal conditions PF_3 (m.p. 151.5 °C, b.p. —101.4 °C) is a gas, PCl_3 (m.p. —90.3 °C, b.p. 75.3 °C) and PBr_3 (m.p. —40.5 °C, b.p. 173.5 °C) are liquids, and PI_3 (m.p. 61 °C, decomposing during boiling) is a low-melting solid. The trihalides of phosphorus are colourless, except PI_3, which is red.

The stability of the compounds decreases in the series PF_3—PCl_3—PBr_3—PI_3 as is shown by the P—Hal bond energy and Gibbs' energy of formation (kJ/mol):

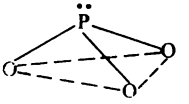
	PF_3 (g)	PCl_3 (g)	PBr_3 (g)	PI_3 (g)
E_{PHal}	490	306	264	184
$\Delta G^\circ_{f,\,298}$	—936	—261	—156	—45

Being donors of an electron pair, phosphorus trihalides readily enter a donor-acceptor interaction with acceptors of electron pairs. The interaction of PCl_3 and BCl_3, for example, yields a low-melting solid with a $PCl_3 \cdot BCl_3$ composition:

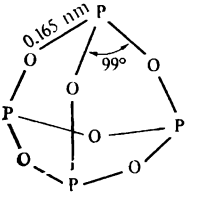


Phosphorus trifluoride and trichloride can act as ligands in complexes of *d* elements.

The phosphorus(III) oxide P_2O_3 exists in several forms built of pyramidal unit cells



The common form of P_2O_3 has a molecular lattice formed by molecules of P_4O_6. It is low-melting (m.p., 23.8 °C, b.p., 175.4 °C) and only slightly soluble in carbon disulphide. The P_4O_6 molecule consists of four PO_3 pyramids linked through the oxygen atoms:



Other forms of P_2O_3 are polymers.

The binary compounds of phosphorus(III) are acidic in chemical nature, as is shown by their hydrolysis

$$P_2O_3 + 3H_2O = 2H_2[PO_3H]$$

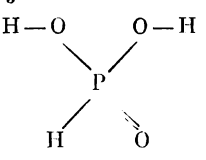
$$PCl_3 + 3H_2O = H_2[PO_3H] + 3HCl$$

and the character of their reaction with basic compounds

$$4NaOH + P_2O_3 = 2Na_2[PO_3H] + H_2O$$

$$3Na_2S + P_2S_3 = 2Na_3[PS_3]$$

Phosphorous acid $H_2[PO_3H]$ is formed during hydrolysis



and the corresponding phosphates(III) are formed in reactions with basic compounds. Derivatives of the $[PO_3H]^{2-}$ ion are called *phosphites*. Most of them, except those of Group I *s* elements, are only slightly soluble in water.

In normal conditions $H_2[PO_3H]$ is a colourless, hygroscopic solid (m.p. 74 °C), readily soluble in water. Its aqueous solution is a dibasic acid (*phosphorous* acid) of medium strength ($K_{a1} = 1.6 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-7}$). As a rule, it is obtained by hydrolising PCl_3.

Phosphorus(III) compounds are quite strong reductants, reducing low-active metals, for example, from solutions of their compounds:

$$HgCl_2 + H_2[\overset{+3}{P}O_3H] + H_2O = \overset{+5}{H_3P}O_4 + Hg + 2HCl$$

Phosphorous acid is oxidised to phosphoric acid by the halogens, nitrogen dioxide and other oxidants. The trihalides are oxidised by fluorine and chlorine to $PHal_5$, by oxygen to $POHal_3$, and so on.

Compounds of phosphorus(V). Phosphorus exhibits its oxidation state of +5 in compounds with the halogens, oxygen, sulphur, and nitrogen:

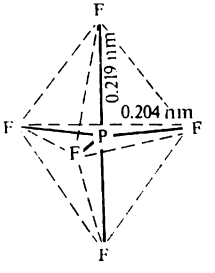
$PHal_5$	P_2O_5	P_2S_5	P_3N_5
PF_6^-	PO_4^{3-}	PS_4^{3-}	PN_2^-

and in mixed compounds

$POHal_3$	$P_2O_3S_2$	PON	$PNHal_2$
$PO_2F_2^-$	$PO_2S_2^{3-}$	PO_2N^{2-}	—

Coordination numbers of four and six, and less frequently five, are characteristic of phosphorus(V). Most of the compounds given above are therefore polymeric since their simplest composition does not correspond to the characteristic coordination number of phosphorus(V).

The phosphorus *pentahalides* $PHal_5$ are relatively simpler in structure, their molecules having the shape of a trigonal bipyramid:



In normal conditions PF_5 is a gas (m.p. −93.7 °C, b.p. 84.6 °C); PCl_5 (sublimes at 159 °C) and PBr_5 (m.p. 106 °C) are solids. The fluoride and chloride are colourless, while PBr_5 is red (or yellow). In accordance with the stable coordination numbers of phosphorus(V) PCl_5 crystals are built of PCl_4^+ and PCl_6^- ions (arranged in the lattice in the same way as Cs^+ and Cl^- in CsCl). Crystals of PBr_5 consist of the PBr_4^+ and Br^- ions, and PCl_4F of PCl_4^+ and F^- ions.

Phosphorus(V) pentahalides are typically acidic compounds and are more or less readily hydrolysed to form acids

$$PHal_5 + 4H_2O = H_3PO_4 + 5HHal$$

In nonaqueous solutions PF_5 reacts with basic fluorides

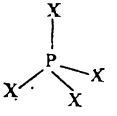
$$KF + PF_5 = KPF_6$$

and forms *hexafluorophosphoric* acid HPF_6 by reaction with liquid HF:

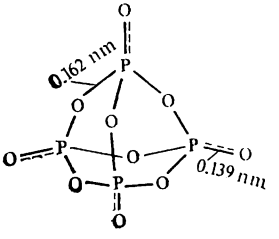
$$HF + PF_5 \rightleftharpoons HPF_6$$

Free HPF_6 is unstable. Its aqueous solution is a very strong acid of the $HClO_4$ type. Hexafluorophosphates can be conveniently obtained by fluorination of oxyphosphates (for example, by the action of BrF_3). Compounds of the fluorophosphate type have not been obtained for the other halogens.

Binary compounds of phosphorus(V) with oxygen, sulphur, and nitrogen are polymeric, all consisting of tetrahedral unit cells of the PX_4 type (PO_4, PS_4, PN_4):



The phosphorus(V) oxide P_2O_5 has the composition of P_4O_{10} in the gaseous state. The P_4O_{10} molecules consist of four PO_4 tetrahedra, each being connected with the three neighbours through the oxygen atoms:

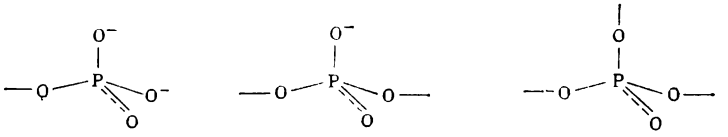


Solid P_2O_5 has several forms differing in arrangement of the PO_4 tetrahedra. When white phosphorus is oxidised, a volatile variety of P_2O_5 is formed with a molecular crystal lattice with P_4O_{10} molecules at its points. This form easily sublimes (at 359 °C) and reacts with exceptional vigour with water. The other forms of P_2O_5 are polymers consisting of endless layers of PO_4 tetrahedra. They melt at higher temperatures (about 580 °C) and are rather less active chemically.

The phosphorus(V) oxide P_2O_5 is obtained by burning phosphorus. The commercial product is a white, snow-like mass, usually consisting of various forms of P_2O_5.

Because of its high affinity for water, P_2O_5 is used for drying gases and liquids. It can absorb water from various substances rendering them anhydrous, and converting HNO_3, for example, into N_2O_5 and even H_2SO_4 into SO_3. It is widely used in chemical synthesis as a good dehydrating agent.

The corresponding *oxyphosphates* are very diverse, which is due to the ability of the PO_4 unit cells to unite with the neighbouring PO_4 tetrahedra through one, two, or three apexes (see Table 10):



In the first case, a dimeric oxyphosphate $P_2O_7^{4-}$ ion is formed, in the second the PO_4 tetrahedra are joined in a chain (open or closed); in the third case a branched chain is formed. The formation of layer

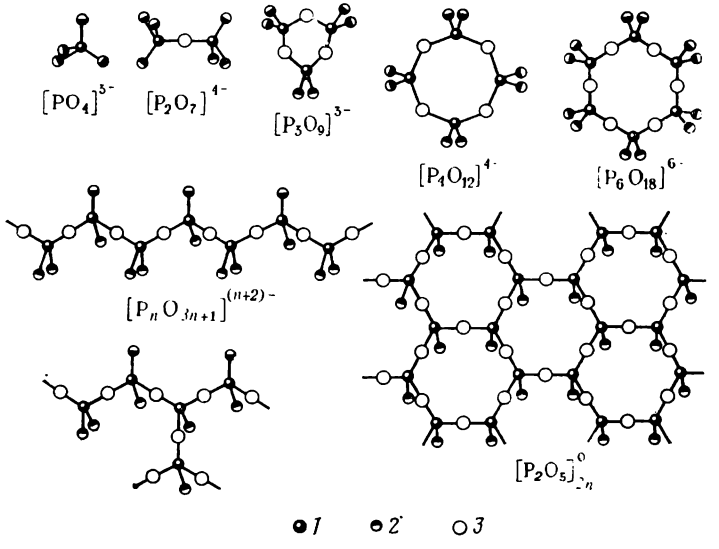


Fig. 160. Structure of oxyphosphate(V) ions and the layer form of P_2O_5:
1—P atom; *2*—terminal O atom; *3*—bridge O atom

forms of P_2O_5 is based on the latter principle. The main types of oxyphosphate(V) ions are shown in Fig. 160. This shows that oxyphosphates(V) are more varied than oxysulphates(VI), which can only have chain structure.

Oxyphosphates(V) with open chains (from two to ten P atoms) are called *polyphosphates*, and those with a cyclic structure, *metaphosphates*. Phosphates with an endless open chain are known as *polymetaphosphates*.

Polyphosphates are salts of anions with the general formula $[P_nO_{3n+1}]^{(n+2)-}$, for example, the dipolyphosphate $\overset{+1}{M}_4P_2O_7$ (*pyrophosphate*) and tripolyphosphate $\overset{+1}{M}_5P_3O_{10}$:

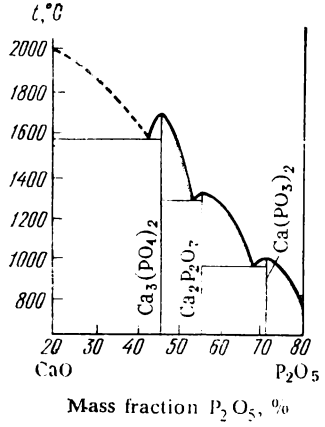
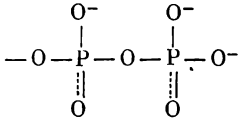
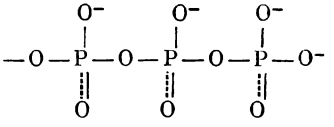


Fig. 161. Phase diagram of a $CaO—P_2O_5$ system



$P_2O_7^{4-}$

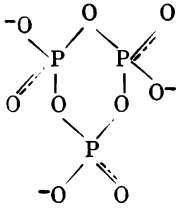
Dipolyphosphate ion



$P_3O_{10}^{5-}$

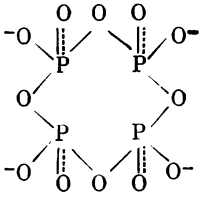
Tripolyphosphate ion

Metaphosphates are salts of anions with the general formula $[P_nO_{3n}]^{n-}$, for example, the trimetaphosphate $\overset{+1}{M}_3P_3O_9$, and tetrametaphosphate $\overset{+1}{M}_4P_4O_{12}$:



$(PO_3)_3^{3-}$

Trimetaphosphate ion



$(PO_3)_4^{4-}$

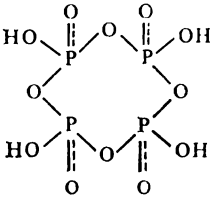
Tetrametaphosphate ion

The simplest oxyphosphates have the following formulas: $\overset{+1}{M}_3PO_4$ and $\overset{+2}{M}_3(PO_4)_2$, $\overset{+1}{M}_4P_2O_7$ and $\overset{+2}{M}_2P_2O_7$, $\overset{+1}{M}PO_3$ and $\overset{+2}{M}(PO_3)_2$. Thus the interaction of CaO with P_2O_5 gives $Ca_3(PO_4)_2$, $Ca_2P_2O_7$ and $Ca(PO_3)_2$ (Fig. 161).

In order to acquaint ourselves with some of the types of phosphoric acid let us consider the hydration of the volatile form of phosphorus(V) oxide P_4O_{10}.

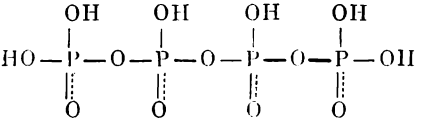
The formation of *tetrametaphosphoric* acid can be regarded as the first state in this hydration:

$$P_4O_{10} + 2H_2O = (HPO_3)_4$$



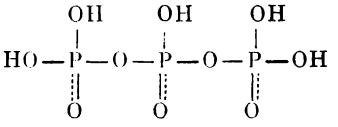
With further hydration, tetrametaphosphoric acid is converted into *tetrapolyphosphoric* acid

$$(HPO_3)_4 + H_2O = H_6P_4O_{13}$$



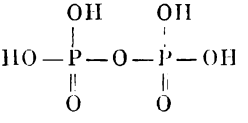
Subsequently the H_3PO_4 molecules are eliminated with the formation first of *tripolyphosphoric* acid

$$H_6P_4O_{13} + H_2O = H_3PO_4 + H_5P_3O_{10}$$



and then of *dipolyphosphoric* (*pyrophosphoric*) acid:

$$H_5P_3O_{10} + H_2O = H_3PO_4 + H_4P_2O_7$$



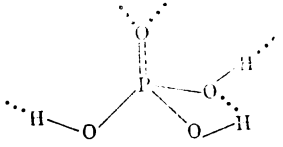
and finally, of *orthophosphoric* acid:

$$H_4P_2O_7 + H_2O = H_3PO_4 + H_3PO_4$$

The hydration of nonvolatile modifications of P_2O_5 is a more complicated business (through the formation of other polyphosphoric acids), but H_3PO_4 is also finally obtained. The conversion of polyphosphoric acids into orthophosphoric acid is accelerated if the solution is boiled, and also in the presence of strong acid.

The simplest representative of hydrogen oxyphosphates is H_3PO_4 whose molecule is a distorted tetrahedron (d_{PO} = 0.152 nm, d_{P-OH} = 0.157 nm, $\angle$O=P—OH 112° and $\angle$HO—P—OH 106°).

In solid and liquid H_3PO_4 (m.p. 42.3 °C) the molecules are connected by hydrogen bonds



which accounts for the increased viscosity of its concentrated solutions.

All hydrogen oxyphosphates are solids readily soluble in water. Their solutions are medium strength acids (for orthophosphoric acid $K_{a1} = 7.52 \times 10^{-3}$, $K_{a2} = 6.31 \times 10^{-8}$, $K_{a3} = 1.26 \times 10^{-12}$). Orthophosphoric acid is produced in huge quantities, usually in the form of a syrupy 85 per cent solution, by the interaction of phosphate minerals and sulphuric acid

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

or by hydration of phosphorus(V) oxide. Orthophosphoric acid is the end product of the hydrolysis of all phosphorus(V) compounds: for example,

$$POHal_3 + 3H_2O = H_3PO_4 + 3HHal$$
$$P_2S_5 + 8H_2O = 2H_3PO_4 + 5H_2S$$
$$H_3PS_4 + 4H_2O = H_3PO_4 + 4H_2S$$

Polyphosphoric acids are formed by the interaction of P_2O_5 and orthophosphoric acid. As will be seen from Fig. 162 the quantity

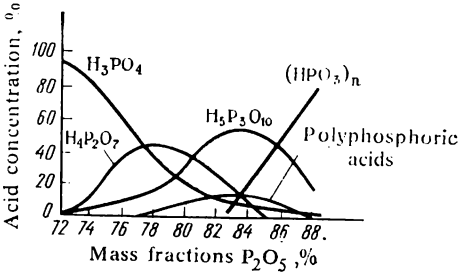


Fig. 162. Composition of phosphoric acids depending on their content in a solution of P_2O_5

of H_3PO_4 falls in the system P_2O_5—H_2O as the amount of P_2O_5 increases, the content of polyphosphoric acids increasing accordingly.

The most important oxyphosphates(V) are derivatives of PO_4^{3-} (*phosphates*), HPO_4^{2-} (*hydrophosphates*), and $H_2PO_4^-$ (*dihydrophosphates*). Only a few phosphates are soluble, in particular, derivatives of Na^+, K^+, NH_4^+. As a rule, phosphates are colourless.

Most phosphates are used as fertilisers; $Ca(H_2PO_4)_2 \cdot H_2O$ for example, is the main constituent of *superphosphate*, while $CaHPO_4 \cdot 2H_2O$, of *precipitated phosphate*. There are also mixed nitrogen-phosphorus fertilisers, known as *ammonium phosphate* fertiliser, a mixture of $(NH_4)H_2PO_4$ and $(NH_4)_2HPO_4$, and *nitrophoska*, a mixture of the former and KNO_3.

Phosphates, in contrast to nitrates, exhibit no oxidising properties.

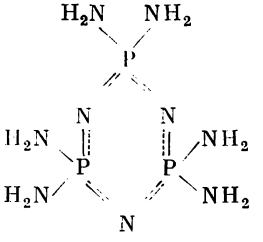
Like P_2O_5, the *sulphide* P_2S_5 also exists in several forms; the simplest is P_4S_{10}, whose structure is similar to that of P_4O_{10}. The oxysulphide $P_4O_6S_4$ has the same structure.

Sulphide phosphates(V) can be obtained by reacting metal sulphides with P_2S_5, or by fusing a metal, red phosphorus, and sulphur. Soluble sulphide phosphates (NH_4^+, K^+, Na^+, etc.) are gradually decomposed by water, liberating H_2S, and subsequently passing into corresponding oxysulphide phosphates, and finally oxyphosphates: for example,

$$Na_3PS_4 \rightarrow Na_3POS_3 \rightarrow Na_3PO_2S_2 \rightarrow Na_3PO_3S \rightarrow Na_3PO_4$$

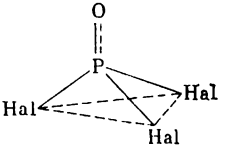
The structure of phosphorus(V) *nitride* P_3N_5 is still unstudied. It is a white solid, very stable chemically, that reacts only when strongly heated (500 °C to 700 °C).

An amorphous compound H_4PN_3 is also known, which is apparently hydrogen metanitride phosphate(V), an analogue of $(HPO_3)_3$:



The PN_2^- anion (which corresponds to the acidic function of P_3N_5) is a polymer and has the structure of the type of SiO_2 (cristobalite). In $LiPN_2$ the Li^+ ions are located in the voids of the trimeric lattice of the PN_2^- coordination ion.

Molecules of $POHal_3$ *oxytrihalides* (*phosphoryl halides*) have the form of a distorted tetrahedron (d_{PO} = 0.145 nm, d_{PF} = 0.152 nm, d_{PCl} = 0.199 nm, ∠HalPHal about 100°):



They are polar ($\mu = 0.6 \times 10^{-29}$ to 1.2×10^{-29} C·m).

In ordinary conditions POF_3 is a gas (m.p. −39 °C); $POCl_3$ is a liquid (m.p. +1 °C, b.p., 107 °C) and $POBr_3$ a solid (m.p. 56 °C). Phosphoryl chloride $POCl_3$ is formed during the hydrolysis of PCl_5 with insufficient water, or by heating a mixture of P_2O_5 and PCl_5:

$$P_2O_5 + 3PCl_5 = 5POCl_3$$

The special tendency of PCl_5 to pass into $POCl_3$ is employed in synthesis, e.g. to convert sulphuric acid H_2SO_4 into chlorosulphonic acid HSO_3Cl and sulphuryl chloride SO_2Cl_2

$$SO_2(OH)_2 + PCl_5 = POCl_3 + SO_2(OH)Cl + HCl$$
$$SO_2(OH)Cl + PCl_5 = POCl_3 + SO_2Cl_2 + HCl$$

Phosphorus(V) oxyfluoride POF_3 corresponds to hydrogen fluophosphates of the type of $H_2[PO_3F]$ and $H[PO_2F_2]$, which are very strong acids in aqueous solutions. They are formed together with HPF_6 during the interaction of P_2O_5 and a solution of HF:

$$2P_2O_5 + 15HF = 2HPF_6 + H_2PO_3F + HPO_2F_2 + 5H_2O$$

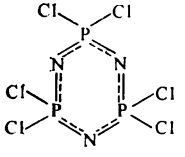
The salts of $H_2[PO_3F]$ resemble sulphates in many respects, while those of $H[PO_2F_2]$ resemble perchlorates. $H[PO_2Cl_2]$ (m.p. −28 °C) is also known.

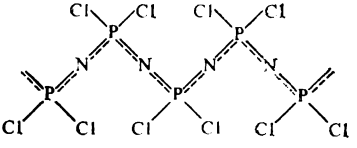
The structure of phosphorus(V) *sulphide halides*, e.g. of the gaseous PSF_3, liquid $PSCl_3$, or solid $PSBr_3$ and PSI_3, is similar to that of $POHal_3$.

Phosphorus(V) *nitride halides* with a $PNHal_2$ composition (*phosphonitryl halides*) are very diverse in structure. Nitride chlorides $PNCl_2$ are formed by heating NH_4Cl and PCl_5 under pressure:

$$NH_4Cl + PCl_5 = PNCl_2 + 4HCl$$

The molecules of $PNCl_2$ consist of PN_2Cl_2 tetrahedra joined together in rings or zig-zag chains:





Most phosphonitryl chlorides $PNCl_2$ are solids, chemically very stable but decomposed by water. High-molecular phosphonitryl chlorides, with their molecules in the form of endless bent chains, resemble rubber in their mechanical properties.

Phosphorus(V) *oxynitride* PON is formed by ammonolysis of $POCl_3$:

$$POCl_3 + 4H_3N = PON + 3NH_4Cl$$

This is an amorphous white powder (stable at temperatures below 750 °C), insoluble in common solvents.

Our survey by no means covers the whole variety of phosphorus compounds. In addition to the inorganic derivatives, there are very many organo-element compounds of phosphorus. A major contribution to their study has been made by A. E. Arbuzov. Phosphorus compounds are widely used in agriculture as fertilisers, weed-killers, and pesticides, in medicine, and in the making of plastics, etc.

5.3. The Arsenic Subgroup

Arsenic As, antimony Sb, and bismuth Bi are full electronic analogues with an s^2p^3 configuration. As the size of the atoms increases in the As—Sb—Bi series, the stable coordination numbers also increase. The oxidation states of arsenic, antimony, and bismuth are -3, $+3$, and $+5$. Because of the special stability of the $6s^2$ configuration, the most characteristic oxidation state of bismuth is $+3$.

The amount of arsenic, antimony, and bismuth in the Earth's crust is comparatively small. They usually occur as sulphides: As_2S_3 (*orpiment*)*, As_4S_4 (*realgar*), Sb_2S_3 (*antimony glance* or *antimonite*), Bi_2S_3 (*bismuth glance* or *bismuthinite*), and also as FeAsS (*arsenopyrite* or *mispickel*).

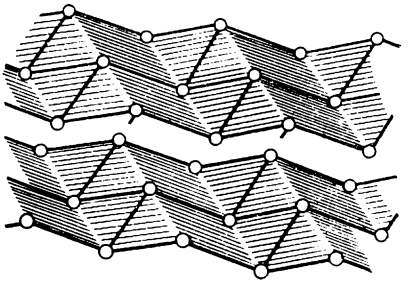


Fig. 163. Layer structure of arsenic, antimony, and bismuth

The simple substances. There is a marked increase in the metallic properties of the simple substances in the N—P—As—Sb—Bi series; the stability of the nonmetallic forms, in particular, diminishes while that of metallic forms increases. Arsenic, like phosphorus, has several allotropic forms. When cooled rapidly, the vapour of As_4 molecules condenses into a nonmetallic form, *yellow arsenic* (density 2.0 g/cm^3), which is isomorphous with white phosphorus, and (like phosphorus) soluble in carbon disulphide. This form is less stable than white phosphorus, and is readily converted into the metallic form, *grey arsenic*, by the effect of light or even of moderate heating.

The nonmetallic form of antimony (*yellow antimony*) is even less stable than yellow arsenic. No nonmetallic form of bismuth is known.

The forms of the elements that are stable in normal conditions (grey arsenic, grey antimony, and bismuth) have a metallic appearance, conduct electricity, but are brittle. They are isomorphous and have a layer structure (Fig. 163) like black phosphorus. Each atom is

* The mineral As_2S_3 (*auripigment*) has an intense lemon-yellow colour, hence its name.

pyramid-bonded with three neighbouring atoms in the layer and has three very close neighbours in the adjacent layer. The difference in internuclear distances within a layer and between adjacent layers decreases in the As—Sb—Bi series (0.063-0.050-0.037 nm), i.e. the spacing characteristics tend to approximate those of metal structures. Because of the similarity of their crystal lattices, antimony forms solid solutions with arsenic and bismuth, but they do not form solid solutions with each other.

Certain constants of the simple substance of *p* elements of Group V are given below:

	N_2	P black	As grey	Sb grey	Bi
Density, g/cm³	0.978*	2.69	5.7	6.68	9.80
M. p., °C	—210	1000**	817***	630	271
B. p., °C	—196	453 (subl.)	615 (subl.)	1637	1559
ΔE, eV	—	1.5	1.2	0.12	metal
d_{EE}, nm					
within layer	—	0.210	0.251	0.288	0.310
between layers	—	0.368	0.314	0.338	0.347
S°_{298}, J/K·mol	199.9	22.7	36.6	45.7	56.9

* In the solid state.
** At 1.8×10^9 Pa.
*** At 3.6×10^6 Pa.

The metallic forms are stable in air or water in normal conditions coming after hydrogen in the electromotive series. Arsenic reacts with concentrated HNO_3 to form arsenic acid:

$$\overset{0}{As} + 5HNO_3 + 2H_2O = \overset{+5}{H_3AsO_4} + 5NO$$

In the same conditions antimony is converted into β-antimonic acid $HSbO_3$ ($Sb_2O_5\cdot nH_2O$):

$$\overset{0}{Sb} + 5HNO_3 = \overset{+5}{HSbO_3} + 5NO + H_2O$$

Bismuth is passivated in concentrated HNO_3 but reacts with dilute nitric acid to give the nitrate, i.e. behaves like a metal:

$$\overset{0}{Bi} + 4HNO_3 = \overset{+3}{Bi(NO_3)_3} + NO + 2H_2O$$

Arsenic, antimony and bismuth are prepared by roasting their natural sulphides, with subsequent reduction of the resulting oxides by carbon:

$$2E_2S_3 + 9O_2 = 6SO_2 + 2E_2O_3$$
$$E_2O_3 + 3C = 2E + 3CO$$

Arsenic, antimony, and bismuth differ substantially in structure from typical metals, and therefore do not usually form solid solutions.

Eutectic mixtures are more characteristic of them. An alloy with a composition 60 per cent Bi and 40 per cent Cd, for example, melts at 144 °C. The widely used *Wood's metal* contains Bi (50 per cent), Pb (25 per cent), Sn (12.5 per cent), and Cd (12.5 per cent) and melts at 65 °C to 70 °C, i.e. below the boiling point of water. An alloy of Bi (41 per cent), Pb (22 per cent), Sn (11 per cent), Cd (8 per cent) and In (18 per cent) melts at 47 °C. Eutectic alloys of bismuth are used in automatic fire extinguishers and as solders.

Arsenic and antimony are used mainly as additives to give greater hardness to lead. An important alloy is *type metal*, which consists of Sb (25 per cent), Pb (60 per cent), and Sn (15 per cent).

Compounds of arsenic (o.s. —3), antimony (o.s. —3) and bismuth (o.s. —3). Examples of compounds in which the oxidation state of arsenic, antimony, and bismuth is —3 are the salt-like *arsenides*, *stibides* (*antimonides*), and *bismuthides* of Group I and II *s* elements (K_3E, Ca_3E_2, Mg_3E_2, etc.). In most other cases, arsenic, antimony and bismuth react with metals to give metallic compounds. The stibides and arsenides of *p* elements and elements of the zinc subgroup are semiconductors. The width of the forbidden band narrows in the series of similar nitrides, phosphides, arsenides, antimonides, and bismuthides, which points to an increase in the proportion of the non-localised bond; for example,

	AlN	AlP	AlAs	AlSb
ΔE, eV	3.8	3.0	2.16	1.6

Most arsenides, antimonides, and bismuthides are quite easily decomposed by acids.

The nonmetal properties of the elements in the As—Sb—Bi series also weaken in their compounds with hydrogen (H_3E). The structure of the H_3E molecules is similar to that of H_3N and H_3P, but as the electron clouds become bigger in the N—P—As—Sb—Bi series, the polarity and strength of the E—H bond diminishes. For the same reason the nonbonding two-electron cloud becomes less oriented in space while the bond angle $\angle$HEH approaches 90°, and there is a decrease in the molecules' dipole moment.

The enthalpies of formation decrease in the same series as follows:

	H_3N	H_3P	H_3As	H_3Sb
d_{EH}, nm	0.102	0.144	0.152	0.171
$\angle$ HEH	107.3°	93.3°	92°	91°
E_{EH}, kJ/mol	380	323	281	256
$\mu_{H_3E} \times 10^{29}$, C·m	0.48	0.19	0.07	0.04
M. p., °C	—77.8	—133.8	—116	—88
B. p., °C	—33	—87.7	—62	—18
$\Delta H^\circ_{f,\,298}$, kJ/mol	—46.19	+5.4	+66.4	+145

In ordinary conditions H_3As (*arsine*), H_3Sb (*stibine*), and BiH_3 (*bismuthine*) are gases with a sharp odour. All of them, but especially

bismuthine, are strongly endothermic. When heated, they readily decompose to form a black deposit with a metallic lustre on the walls of the vessel (the simple substances As, Sb and Bi). Stability falls in the $H_3As—H_3Sb—BiH_3$ series, so that bismuthine has been little studied. All these compounds are strong reductants.

H_3E are formed by the action of dilute acids on arsenides, stibides, and bismuthides

$$Mg_3E_2 + 6HCl = 3MgCl_2 + 2H_3E$$

and by the action of zinc on acidified solutions of the compounds

$$As_2O_3 + 6Zn + 12HCl = 2H_3As + 6ZnCl_2 + 3H_2O$$

Arsine (and to a lesser degree stibine and bismuthine) is very toxic. Since zinc almost always contains small amounts of arsenic, it is dangerous to inhale the hydrogen liberated during its reaction with acids.

Dipole moment of arsine and stibine nears zero, which indicates that the E—H bond is almost nonpolar, while a nonbonding electron pair is only slightly space oriented.

The electron-donating capacity of molecules decreases in the series $H_3N—H_3P—H_3As—H_3Sb—BiH_3$. Thus, while ammonia derivatives are quite stable, the *arsonium* AsH_4^+ ion has only been detected by infra-red spectroscopy (in a mixture of H_3As and HI at low temperatures). SbH_4^+ and BiH_4^+ ions have not been discovered.

Compounds of arsenic(III), antimony(III) and bismuth(III). The atoms of As, Sb, and Bi retain their nonbonding electron pair in their +3 oxidation state. Their coordination numbers are 3, 4, 5, and 6, which correspond to a trigonal AB_3E type pyramid (see Fig. 51*b*), a distorted AB_4E type tetrahedron (see Fig. 51*e*), a tetragonal AB_5E type pyramid (see Fig. 51*i*), and a distorted AB_6E type octahedron, respectively.

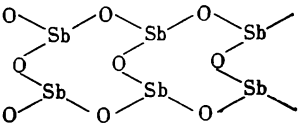
A +3 oxidation state of arsenic and its analogues is displayed in the trihalides $EHal_3$, oxides E_2O_3, and sulphides E_2S_3. The binary compounds and hydroxides of E(III) are amphoteric. Anion complexes corresponding to the acidic characteristics of E(III) compounds have the following composition

$EHal_3$	E_2O_3	$E(OH)_3$	E_2S_3
$EHal_4^-$	EO_2^-	$E(OH)_4^-$	ES_2^-

The acidic properties decrease and the basic ones increase in the series of similar compounds of As(III)—Sb(III)—Bi(III).

The *oxides* E_2O_3 are obtained by direct interaction of the simple substances; Sb_2O_3 can also be prepared by oxidising antimony by dilute HNO_3, and Bi_2O_3 by thermal decomposition of $Bi(NO_3)_3$.

The structure of the *oxides* changes substantially in the transition from As(III) to Bi(III). Crystals of the low-melting forms of As_2O_3 and Sb_2O_3 (like P_2O_3) have molecular lattices consisting of E_4O_6 molecules, which in turn consist of four interconnected EO_3 pyramids (see p. 374). In the high-melting form of Sb_2O_3 the SbO_3 pyramids are joined in endless double chains:



Bismuth(III) oxide Bi_2O_3 has a coordination lattice with a distorted octahedral-tetrahedral coordination of the atoms. These differences in structure account for the different character of the oxides:

	As_2O_3	Sb_2O_3	Bi_2O_3
Colour	white	white	yellow
M. p., °C	274	656	820
B. p., °C	460	1456	1010 (subl.)
$\Delta H^\circ_{f,\,298}$, kJ/mol	−653	−699	−578
$\Delta G^\circ_{f,\,298}$, kJ/mol	−574	−619	−498
Solubility in water, mol/l	9×10^{-2}	3×10^{-5}	2×10^{-8}

As_2O_3 (*white arsenic*) is mainly an acidic oxide. It is soluble in water and alkalis but, unlike P_2O_3, also reacts with hydrohalic acids

$$As_2O_3 + 2H_2O = 2H_3AsO_3$$
$$As_2O_3 + 8HCl = 2HAsCl_4 + 3H_2O$$

Sb_2O_3 is practically insoluble in water but reacts with alkalis and hydrochloric acid.

The interaction of As_2O_3 and Sb_2O_3 with alkaline solutions gives hydroxyarsenates(III) (*hydroxyarsenites*) and hydroxystibates(III) (*hydroxyantimonites*):

$$E_2O_3 + 2KOH + 3H_2O = 2K[E(OH)_4]$$

Bi_2O_3, on the contrary, readily reacts with acids to form numerous salts of Bi(III). It is insoluble, however, in water and hardly reacts with alkalis.

The properties of the *hydroxides* change in a similar way. In contrast to H_3PO_3, $As(OH)_3$ and $Sb(OH)_3$ are amphoteric: acidic properties predominate in the former and basic in the latter. The acidic and basic ionisation of $E(OH)_3$ in solution is slightly pronounced.

$As(OH)_3$ has not been isolated in the free state; in an aqueous solution it behaves like a weak acid H_3AsO_3 (*arsenous acid*).

The hydroxides of Sb(III) and Bi(III) are practically insoluble in water. They are prepared in the form of white precipitates with a variable $E_2O_3 \cdot nH_2O$ composition either by the action of alkalis on

cationic derivatives of E(III)

$$Bi(NO_3)_3 + 3KOH = Bi(OH)_3\downarrow + 3KNO_3$$

or acids on the anionic derivatives of E(III)

$$Na[Sb(OH)_4] + HCl = NaCl + Sb(OH)_3\downarrow + H_2O$$

The fusing of E_2O_3 or $E(OH)_3$ with alkalis as a rule yields polymeric meta-arsenates(III) (*meta-arsenites*) and metastibates(III) (*meta-antimonites*) of $\overset{+1}{M}EO_2$ composition. Oxybismuthates(III) are unstable.

The metastibates(III) of an $\overset{+2}{M}(SbO_2)_2$ type (M = Mg, Zn, Mn, Fe, Co, and Ni), obtained by fusing the corresponding oxides, are mixed oxides formed by chains of MO_6 octahedra linked with chains of SbO_3 pyramids (d_{SbO} =0.201 nm and 0.187 nm, ∠OSbO = 101° and 95°, see the structure of Pb_3O_4 in Fig. 176).

A weakening of acidic character can also be seen in the E_2S_3 *sulphides* series. Yellow As_2S_3, orange Sb_2S_3, and blackish brown Bi_2S_3 are solids insoluble in water.

The unit cell of the sulphides is an ES_3 trigonal pyramid. The structure of As_2S_3 (As_4S_6) is similar to that of As_2O_3. Sb_2S_3 and Bi_2S_3 are ribbon polymers.

	As_2S_3	Sb_2S_3	Bi_2S_3
M. p., °C	310	550	685
B. p., °C	707	1180	Subl.

The sulphides are formed by direct interaction of the simple substances, or by the action of hydrogen sulphide on soluble E(III) compounds in an acidic medium

$$2Na[As(OH)_4] + 3H_2S + 2HCl = 2NaCl + As_2S_3\downarrow + 8H_2O$$

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3\downarrow + 6HNO_3$$

The sulphides of As(III) and Sb(III) are predominantly acidic compounds, readily soluble in the presence of basic sulphides with formation of sulphide arsenates(III) and sulphide stibates(III) of the type of $\overset{+1}{M}ES_2$ and $\overset{+1}{M}_3ES_3$

$$E_2S_3 + (NH_4)_2S = 2NH_4ES_2$$

As_2S_3 and Sb_2S_3 are also soluble in alkalis.

Bismuth(III) sulphide Bi_2S_3 does not exhibit acidic properties in solution and only reacts with basic sulphides when fused with them.

Gibb's energies of formation are comparatively low in E_2S_3 compounds which are quite readily converted into E_2O_3, EF_3, and ECl_3 when oxidised by oxygen, fluorine, and chlorine; for example,

$$2Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$$

Unlike As_2S_3, Sb(III) and Bi(III) sulphides are soluble in concentrated hydrochloric acid:

$$Sb_2S_3 + 8HCl \rightleftharpoons 2HSbCl_4 + 3H_2S$$

Sulphide arsenates(III) (*thioarsenites*) and sulphide stibates(III) (*thioantimonites*) are quite stable in the solid state but the corresponding thio acids decomposed the moment they are formed:

$$2NH_4AsS_2 + 2HCl = 2HAsS_2 + 2NH_4Cl$$

$$2HAsS_2 = As_2S_3 + H_2S$$

$$2NH_4AsS_2 + 2HCl = 2NH_4Cl + As_2S_3 + H_2S$$

The *trihalides* of arsenic subgroup elements $EHal_3$ are obtained by interaction of the simple substances without sufficient halogen.

The trihalide $EHal_3$ molecules (like $PHal_3$) have a pyramidal structure. The internuclear distance increases and the bond energies, enthalpies, and Gibbs' energies diminish in the EF_3—ECl_3—EBr_3—EI_3 series in accordance with the increase in size of the halogen atoms:

	AsF_3	$AsCl_3$	$AsBr_3$	AsI_3
$d_{As\ Hal}$, nm	0.171	0.216	0.233	0.255
$E_{As\ Hal}$, kJ/mol	464	293	242	180
ΔH_f°, kJ/mol	—921	—305	—198	—58
ΔG_f°, kJ/mol	—908	—268	—162	—66
M. p., °C	—6	—16	31	144
B. p., °C	57	130	221	403

In most of these trihalides the crystal lattices are molecular. The melting point of bismuth trifluoride, which has a coordination lattice, is the highest (730 °C).

The halides of As(III), like E_2O_3 and E_2S_3, are acidic compounds; the halides of Sb(III) and Bi(III) also have the properties of salts.

Hydrolysis of $AsHal_3$ yields acids; in contrast to $PHal_3$, however, the hydrolysis of $AsHal_3$ is reversible:

$$AsCl_3 + 4H_2O \rightleftharpoons H[As(OH)_4] + 3HCl$$

Hydrolytic decomposition of Sb(III) and Bi(III) halides also prevails over their electrolytic dissociation. The hydrolysis proceeds vigorously to oxyhalides, for example,

$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2HCl$$

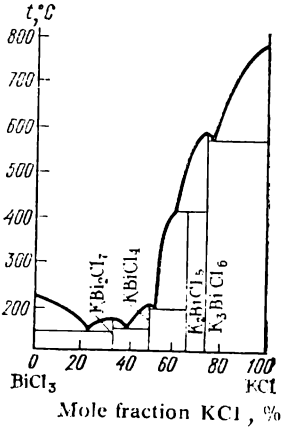
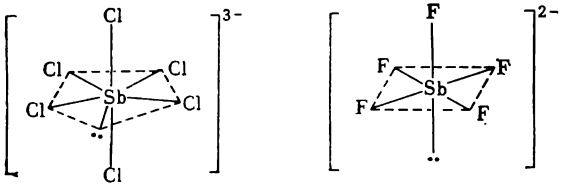


Fig. 164. Phase diagram of a $BiCl_3$—KCl system

The acidic nature of $EHal_3$ is also exhibited in their reaction with basic halides, during which halogen arsenates(III), stibates (III), and bismuthates(III) are formed respectively.

Their composition is usually $\overset{+1}{M}_3[EHal_6]$, $\overset{+1}{M}_2[EHal_5]$ and $\overset{+1}{M}[EHal_4]$ (Fig. 164).

The $[SbHal_6]^{3-}$ ion has the form of a distorted octahedron, while the $[SbF_5]^{2-}$ ion (like IF_5) is a square pyramid:



The arrangement of the bonds in the tetrameric $[SbCl_4^-]_4$ ion are the same as in the SbF_5^{2-} ion.

The *oxyhalides* of Sb(III) and Bi(III) with a EOHal composition are ordinarily solids, insoluble in water. They have coordination layer lattices and differ in structure from the analogous oxyhalides of phosphorus(III) and arsenic(III). The arrangement of the atoms in a layer of BiOCl crystal is shown in Fig. 165.

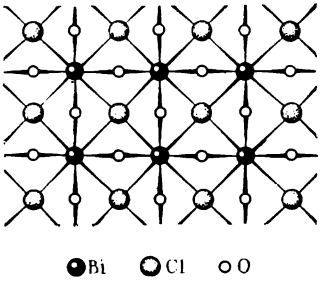


Fig. 165. Structure of a layer of a crystal of BiOCl
The atoms of O and Cl are above and below the plane of Bi atoms respectively

The weakening of nonmetallic character in the As—Sb—Bi series is also displayed in the changing stability of E(III) salts and salt-like compounds. They are unstable with As(III), and have not been obtained in the free state. The known Sb(III) compounds include the sulphate $Sb_2(SO_4)_3$, the nitrate $Sb(NO_3)_3$, and certain others. They decompose vigorously in water. The complex stibates(III) of Group I *s* elements, e.g. the sulphate stibate(III) $\overset{+1}{M}[Sb(SO_4)_2]$ are more stable.

The salts of Bi(III) are quite varied and stable. Their acidic properties are displayed in the character of their hydrolysis (which prevails over electrolytic dissociation):

$$Bi(NO_3)_3 + H_2O \rightleftharpoons BiONO_3 + 2HNO_3$$

and in their ability to form derivatives of an $\overset{+1}{M}[Bi(SO_4)_2]$ and $\overset{+1}{M}[Bi(NO_3)_4]$ type.

As(III) compounds are quite easily oxidised, As_2S_3, for instance, being oxidized by ammonium persulphide

$$As_2S_3 + 2(NH_4)_2S_2 = As_2S_5 + 2(NH_4)_2S$$

and As_2O_3 by nitric acid

$$3As_2O_3 + 4HNO_3 + 7H_2O = 6H_3AsO_4 + 4NO$$

Reducing activity is less pronounced in derivatives of Sb(III), but Sb_2S_3 is also oxidised by ammonium persulphide. Compounds of Bi(III) can only be oxidised by the strongest oxidising agents in a strongly alkaline medium: e.g.

$$BiCl_3 + Cl_2 + 6KOH = KBiO_3 + 5KCl + 3H_2O$$

Compounds of arsenic(V), antimony(V), and bismuth(V). The stability of compounds decreases in the As(V)—Sb(V)—Bi(V) series and the inner periodicity can be seen in the variation of their properties (see Fig. 131). In the survey of the bromine and selenium subgroups (see Fig. 137) it was shown that the highest oxidation state in these subgroups is most characteristic of *p* elements of the fifth period, i.e. of I and Te. The highest oxidation state is the least stable one for *p* elements of the sixth period, i.e. for At and Po. The same pattern, although less pronounced, is displayed in the arsenic subgroup: the +5 oxidation state is most characteristic of Sb and less characteristic of As, it is unstable with Bi.

BiF_5 has only been obtained with bismuth(V); oxides E_2O_5 and sulphides E_2S_5 are also known for arsenic(V) and antimony(V), and a chloride $SbCl_5$ for antimony(V):

AsF_5	SbF_5	BiF_5
$(AsCl_5)$	$SbCl_5$	$(BiCl_5)$
As_2O_5	Sb_2O_5	(Bi_2O_5)
As_2S_5	Sb_2S_5	(Bi_2S_5)

The binary compounds of arsenic(V) and its analogues are acidic in nature. They form corresponding anion complexes, the simplest being $EHal_6^-$, EO_4^{3-}, and $E(OH)_6^-$.

The E_2O_5 *oxides* are solids in normal conditions; As_2O_5 resembles P_2O_5 in structure and properties; it is quite readily soluble in water:

$$As_2O_5 + 3H_2O = 2H_3AsO_4$$

Sb_2O_5 (yellow) is barely soluble in water and more so in alkaline solutions:

$$Sb_2O_5 + 2KOH + 5H_2O = 2K[Sb(OH)_6]$$

The oxyarsenates(V) and oxystibates(V) formed by fusing As_2O_5 and Sb_2O_5 with alkalis and metal oxides are mostly polymers.

The structure of oxyarsenates is usually like that of oxyphosphates(V). An octahedral SbO_6 unit cell is most characteristic of oxystibates(V), $\overset{+1}{M}SbO_3$, $\overset{+3}{M}SbO_4$ and $\overset{+2}{M}_2Sb_2O_7$. The structure of oxybismuthates(V) has not been adequately studied. Polymeric bismuthates usually have an $\overset{+1}{M}BiO_3$ composition.

Tetraoxyarsenates of the $\overset{+1}{M}_3AsO_4$ type and hexahydroxystibates of the $\overset{+1}{M}[Sb(OH)_6]$ type are usually precipitated from solutions.

Arsenates, stibates, and bismuthates (like phosphates) are normally only slightly soluble in water.

The only corresponding hydrogen compound obtained in the free state is hydrogen oxyarsenate(V) H_3AsO_4 (*orthoarsenic acid*); it is a solid, soluble in water. The acid is prepared by oxidising As or As_2O_3 by nitric acid. Arsenic acid ($K_1 = 6 \times 10^{-3}$) is weaker than phosphoric acid. When attempts are made to isolate antimonic acids a precipitate of indefinite $Sb_2O_5 \cdot nH_2O$ composition is formed. Bismuthic acids have also not been obtained in the free state.

The *sulphides* E_2S_5 resemble E_2O_5 in many respects. Yellow As_2S_5 and orange Sb_2S_5 do not react with water. Being acidic, they dissolve in the presence of basic sulphides and under the action of alkalis

$$E_2S_5 + 3Na_2S = 2Na_3ES_4$$

The E_2S_5 sulphides can be obtained either through interaction of the simple substances, or by precipitation during the action of H_2S on E(V) derivatives in an acid medium:

$$2Na_3AsO_4 + 5H_2S + 6HCl = As_2S_5 + 6NaCl + 8H_2O$$

The corresponding hydrogen sulphide arsenates(V) and sulphide stibates(V) (*thioantimonates*) are unstable in the free state.

The molecules of $EHal_5$ *pentahalides* like $PHal_5$, have a trigonal bipyramid shape (see Fig. 49*e*).

In normal conditions AsF_5 is a gas (m.p. −80 °C, b.p. −53 °C). SbF_5 (m.p. 8 °C, b.p. 142 °C) and $SbCl_5$ (m.p. +3 °C, b.p. 140 °C) are liquids, and BiF_5 (m.p. 151 °C, b.p. 230 °C) a solid. The steep rise in melting and boiling points in the transition from AsF_5 to SbF_5 is due to the association of SbF_5 molecules in polymer chains formed by octahedral SbF_6 unit cells (—SbF_4—F—SbF_4—F—). The pentahalides are typical acidic compounds, reacting with water to give acids; with basic halides they form halide arsenates(V) and halide stibates(V):

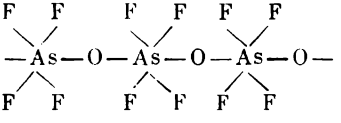
$$KF + EF_5 = K[EF_6]$$

The pentafluorides EF_5 are strong acceptors of fluoride ions. In reactions with EF_5, even compounds like HF, O_2F_2, N_2F_2, N_2F_4, ClF_5, and others exhibit basic properties (see pp. 322 and 368):

$$2HF + SbF_5 \rightleftarrows FH_2^+ + SbF_6^-$$

$$ClF_5 + SbF_5 = [ClF_4]^+[SbF_6]^-$$

Derivatives of $[AsCl_6]^-$, $[SbBr_6]^-$, $[BiOF_5]^{2-}$, $[AsF_5(OH)]^-$, and other complexes are also known. Derivatives of the $\overset{+1}{M}[EOF_4]$ type are formed by polymeric ions in the form of a chain of octahedral unit cells



Bismuth(V) compounds are strong oxidising agents. They convert Mn(II) to Mn(VII). For example

$$2Mn^{2+} + 5BiO_3^- + 14H^+ = 5Bi^{3+} + 2MnO_4^- + 7H_2O$$

Bismuth(V) compounds are less strong oxidising agents, but Sb_2O_5 can oxidise concentrated hydrochloric acid in the following reversible reaction

$$Sb_2O_5 + 10HCl \rightleftharpoons 2SbCl_3 + 2Cl_2 + 5H_2O$$

The applications of arsenic, antimony, and bismuth compounds are most varied. Derivatives of As are used in agriculture as a main means of pest control; Na_3AsO_4, $Ca_3(AsO_4)_2$, $Ca(AsO_2)_2$, etc., are used, for example, as insecticides. Organic derivatives of arsenic and As_2O_3 and $KAsO_2$ are of great value in medicine (for anaemia, exhaustion) and are employed in stomatological practice. Derivatives of As, Sb and Bi are also used in the manufacture of ceramics, and in other fields.

Compounds of antimony and bismuth, especially of arsenic, are *poisonous!*

CHAPTER 6

Group IV *p* Elements

Carbon C, silicon Si, germanium Ge, tin Sn, and lead Pb are *p* elements of Group IV of the periodic system. In accordance with the electron configuration of their atoms

C	$1s^22s^22p^2$
Si	$2s^22p^63s^23p^2$
Ge	$3s^23p^63d^{10}4s^24p^2$
Sn	$4s^24p^64d^{10}5s^25p^2$
Pb	$4s^24p^64d^{10}4f^{14}5s^25p^65d^{10}6s^26p^2$

carbon and silicon are *typical elements* and germanium, tin, and lead are put in a *germanium subgroup.*

The main characteristics of Group IV *p* elements are as follows:

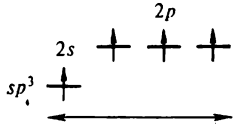
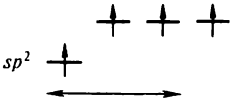
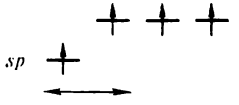
	$_6$C	$_{14}$Si	$_{32}$Ge	$_{50}$Sn	$_{82}$Pb
Atomic mass	12.01115	28.086	72.59	118.69	207.19
Valence electrons	$2s^22p^2$	$3s^23p^2$	$4s^24p^2$	$5s^25p^2$	$6s^26p^2$
Metallic radius of atom, nm	0.077	0.134	0.139	0.158	0.175
Covalent radius of atom, nm	0.077	0.117	0.122	0.140	0.146

	$_{6}C$	$_{14}Si$	$_{32}Ge$	$_{50}Sn$	$_{82}Pb$
Conventional E^{2+} ion radius, nm	—	—	0.065	0.102	0.126
Conventional E^{4+} ion radius, nm	0.020	0.039	0.044	0.067	0.076
$E^0 \rightarrow E^+$ ionisation energy, eV	11.26	8.15	7.90	7.34	7.42
Abundance, mole per cent	0.15	20.0	2×10^{-4}	7×10^{-4}	1.6×10^{-4}

It will be obvious from this table (and from Fig. 12) that carbon differs essentially from the other *p* elements of this group in its high ionisation energy. Carbon is a typical nonmetal. Ionisation energy decreases in the C—Si—Ge—Sn—Pb series, so that the nonmetal character of the elements weakens and their metallic properties increase. A secondary periodicity can be seen in the change in properties of the atoms and compounds of this series (see Figs. 18 and 131).

6.1. Carbon

Depending on the number of σ bonds, the coordination number of carbon is four (sp^3 hybridisation), three (sp^2 hybridisation) or two (*sp* hybridisation of valence orbitals).

Hybridisation of carbon's atomic orbitals	Spatial arrangement of σ bonds	Typical compounds
	Tetrahedral	Diamond, CH_4, $CHal_4$
	Triangular	Graphite, C_6H_6, CO_3^{2-}
	Linear	Carbin, CO_2, CS_2

In the most of its compounds carbon is tetravalent. Its oxidation states are −4, +4, and +2.

In contrast to all other elements, the number of valence electrons in carbon is equal to the number of the valence orbitals, which is

a main reason for the high stability of the C—C bond and carbon's exceptional tendency to form homochains. Bond energy decreases steeply in the series from carbon to nitrogen:

	—C—C—	—N—N—	—O—O—	:F—F:
	$H_3C—CH_3$	$H_2N—NH_2$	HO—OH	F—F
E_{EE}, kJ/mol	374	250	210	159

which is due to repulsion of the nonbonding electron pairs of the nitrogen atoms. Homochain molecules containing the C—C bond are most varied, e.g. linear, branched, closed, cyclic. These numerous compounds of carbon are the field of organic chemistry.

Carbon occurs in nature in the form of two stable isotopes, ^{12}C (98.892 per cent) and ^{13}C (1.108 per cent). Its abundance in the Earth's crust is 0.15 mole per cent. A certain amount of the beta-radioactive isotope ^{14}C is also produced in the atmosphere through the action of cosmic rays:

$$^{14}_{7}N + ^{1}_{0}n = ^{14}_{6}C + ^{1}_{1}H$$

The age of vegetable remains can be determined from their ^{14}C content. Radioactive isotopes with mass numbers from 10 to 16 have also been obtained. Carbon occurs in the crust in the form of its minerals (primarily $CaCO_3$ and $MgCO_3$), coal, petroleum, and also graphite and (more rarely) diamonds. Carbon is the main constituent of animal and vegetable matter.

The simple substances. In contrast to the second period elements discussed, the simple substances of which have the molecular structure F_2, O_2, N_2, the simple substances of carbon have a polymeric structure. The multiple bonds of diatomic molecules O_2 and N_2 are much stronger than the σ bonds of homochains (kJ/mol):

O ⋮⋮ O	—O—O—O—	N ≡ N	—N—N—N—
494	210 210	946	250 250

The electron configuration of the diatomic molecule C_2 (see p. 63)

$$[\sigma_s]^2[\sigma_s^*]^2[\pi_{x,y}]^4$$

shows that the atoms in the molecules are linked by two bonds. The bond in the C_2 molecule is weaker than two σ bonds in homochains (kJ/mol)

C=C	—C—C—C—
627	374 374

In accordance with the characteristic hybridisation states, carbon atoms can unite into polymeric formations with coordination (sp^3), layer (sp^2), and linear (sp) structures. These correspond to the three simple substances of carbon, namely, *diamond*, *graphite* and *carbin*.

Diamond. Diamond is a crystalline substance with an atomic cubic coordination lattice (Fig. 166). Because of sp^3 hybridisation, each carbon atom in diamond forms equivalent stable σ bonds with four neighbouring atoms, which explains its exceptional hardness and

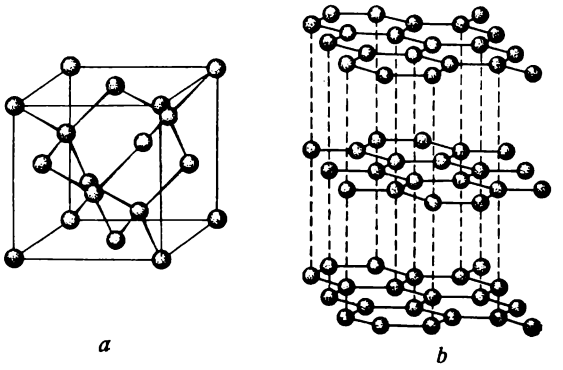


Fig. 166. Structure of (*a*) diamond and (*b*) of graphite

the absence of electron conductivity in normal conditions (ΔE = = 5.7 eV). Its very low entropy (only 2.4 J/K·mol) is also evidence of its rigid structure.

Graphite is a crystalline substance with a hexagonal layer structure (Fig. 166). In accordance with sp^2 hybridisation, the carbon atoms are united in $C_{2\infty}$ macromolecules that are endless layers of six-membered rings. The sp^2 hybridisation is stabilised in this case

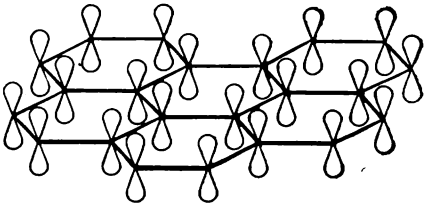


Fig. 167. Orientation of the *p* orbitals of carbon atoms in a $C_{2\infty}$ macromolecule

by a delocalised π bond formed through the fourth electron of each atom in the macromolecule (Fig. 167). The π bond in graphite is delocalised within the limits of the whole macromolecule, which explains the electrical conductivity, grey colour, and metallic lustre of graphite. The carbon layers are united in the crystal lattice mainly through intermolecular forces. The strength of the chemical bonds is much higher within the macromolecule (716 kJ/mol) than

between the layers (only 17 kJ/mol). Graphite is therefore soft and easily disintegrates into layers. Its chemical activity is a little higher than that of diamond, but its density is lower (2.1 to 2.5 g/cm^3 against 3.5 g/cm^3 in diamond), while its entropy, on the contrary, is higher (5.74 J/K·mol).

Carbin is a black powder (density, 1.9 to 2 g/cm^3) with a hexagonal lattice built of rectilinear C_∞ chains in which each atom forms two σ and two π bonds. The *sp* hybridisation of the carbon orbitals corresponds to a chain arrangement of its atoms:

$$-C\equiv C-C\equiv C-C\equiv \text{ (polyine) or } =C=C=C=C=C= \text{ (polycumulene)}$$

The existence of two linear structures has been proved by physical and chemical methods (in particular, polyine is converted into oxalic acid during ozonisation and polycumulene into carbonic acid). Carbin is a semiconductor ($\Delta E = 1$ eV). Its electrical conductivity increases steeply when it is exposed to light. It has been only recently synthesised by Soviet chemists (in the early 1960s), and was later found in nature.

In accordance with the increasing bond order between carbon atoms in the diamond—graphite—carbin series the internuclear distance d_{CC} decreases: 0.155—0.142—0.128 nm (Fig. 168). The distance between layers in graphite is 0.335 nm, and between chains in carbin 0.295 nm.

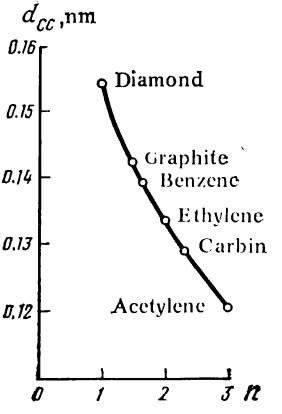


Fig. 168. Effect of bond multiplicity (n) on internuclear distance d_{CC}

The forms of carbon can be arranged in the following order in accordance with decreasing entropy: $S_{carbin} - S_{graphite} - S_{diamond}$. Comparison of the heats of combustion of diamond (—395 kJ/mol), graphite (—394 kJ/mol), and carbin (—360 kJ/mol) shows that the most stable form is carbin and the least stable one diamond. Because of the very high activation energy, the forms of carbon can only be converted into one another in special conditions. Diamond, for instance, is converted into graphite when heated to between 1000 °C and 1500 °C (in the absence of air). The reverse transition of graphite into diamond

$$C_{graphite} \rightarrow C_{diamond}, \quad \Delta H > 0, \quad \Delta S < 0$$

requires very high pressure (6×10^9 - 10×10^{10} Pa) because of the insignificant reduction of volume (in accordance with Le Chatelier's principle). The increase in temperature is unfavourable for a shift of equilibrium but it is required in order to reach an acceptable rate of the process. The reaction temperature is approximately 2000 °C.

A method of producing diamond at low pressures has recently been devised, by which a diamond seed is placed in an atmosphere of gaseous hydrocarbons (methane, ethane) and the temperature is raised

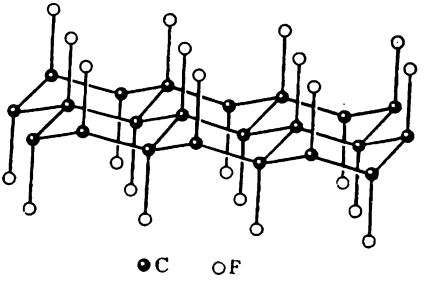


Fig. 169. Structure of carbon fluoride CF

to about 1000 °C. A diamond powder or crystal 'whiskers' are obtained in this way.

The *black graphite* or *coal* obtained through thermal decomposition of organic compounds, is fine graphite. The most important commercial grades of black graphite are *coke*, *wood charcoal*, *bone* or *animal charcoal*, and *soot*. All these forms have high melting points.

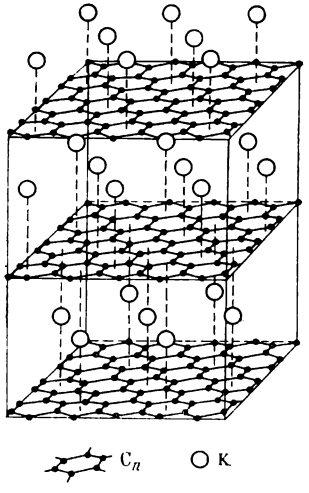


Fig. 170. Structure of KC_8 graphitide

Elementary carbon is quite inactive at normal temperatures, but at high temperatures it can react directly with many metals and nonmetals, and possesses reducing properties that are widely used in metallurgy. Its oxidising properties are weak.

Because of their differences in structure, diamond, graphite, and carbin behave differently in chemical reactions. Reactions forming crystalline compounds in which the macromolecular layers of $C_{2\infty}$ act as independent radicals are characteristic of graphite.

During reactions with fluorine, for instance, the nonlocalised π bond of graphite breaks and two-electron C–F σ bonds arise. The *fluoride of carbon* with a CF composition is formed in the extreme case (Fig. 169), a conversion of carbon from the sp^2 to the sp^3 hybrid state taking place. Since all bonds in carbon fluoride are localised, it is a dielectric. It is a colourless substance, transparent, and chemically inert, and does not react even with concentrated alkalis or acids. It is used as a lubricating material. Further fluorination converts CF into CF_4. Diamond is oxidised directly

to CF_4 by fluorine when heated. This different attitude to fluorine is the basis of a method of separating graphite from synthetic diamond.

When graphite is heated in the vapour or a melt of an alkali metal (Cs, Rb, K) inclusion compounds or *graphitides* of the metal are formed in which the hexagonal lattices of $C_{2\infty}$ act as the anion. The structure of potassium graphitide KC_8 is shown in Fig. 170. Graphitides $\overset{+1}{M}C_8$ are quite reactive copper-red substances that ignite spontaneously in air and explode on contact with water.

Inclusion compounds are also formed through the interaction of graphite and other substances (HNO_3, H_2SO_4, Cl_2, $FeCl_3$, etc.).

Graphite is used in the manufacture of electrodes and crucibles, as a lining for furnaces and industrial electrolysis tanks, etc., and as a neutron moderator in nuclear reactors. It is also used as a lubricant, in pencils, etc. The exceptional hardness of diamond makes it widely used for working especially hard materials, drilling oil wells, drawing wires, and so on. Diamonds of perfect shape (gem stones) are used as jewellery.

Because of their high adsorbtive capacity, wood and animal charcoals are used to purify substances of admixtures. Carbon black is used in the manufacture of black rubber, paints, Indian ink, etc.

A combination of carbon atoms in different hybrid states in a single polymeric structure yields numerous amorphous forms of carbon. A typical example is what is called *carbon fibres* in which structural fragments of diamond, graphite, and carbin are connected at random. They are obtained by thermal decomposition of certain carbon-containing compounds. Carbon fibres are a new constructional material with unique properties not found in ordinary forms of carbon. They are refractory (remaining solid at temperatures up to 3700 C), have a lower density than most other refractory materials (under 1.5 g/cm^3), conduct electricity, and are mechanically strong. They are stable under the action of many aggressive media (molten alkalis and salts, acids, oxidising agents, etc.). Carbon fibre articles of various shape (tubes, cylinders, cups, etc.) are produced by thermal decomposition of carbon-containing compounds or by pressing carbon fibres. The unique properties of this material enable it to be widely used in nuclear power stations, the electrochemical industry, and to make apparatus for especially aggressive media. The fibres, being of low density, and having high tensile strength and thermal stability, can be used in aerospace applications and other fields.

Compounds of carbon in a negative oxidation state. Carbon forms *carbides* with elements less electronegative than itself. Since it is characteristic of carbon to form homochains, the composition of most carbides does not correspond to the oxidation state of carbon -4; covalent, ionic-covalent, and metallic carbides are distinguished, according to the type of chemical bond.

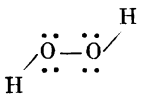
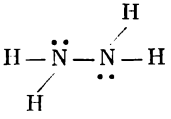
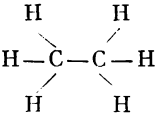
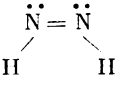
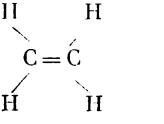
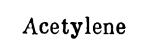
The covalent carbides of silicon SiC and boron B_4C are very hard, refractory, chemically inert polymers.

Methane CH_4 can be regarded as the simplest covalent carbide. Its molecule (see Fig. 43) has a tetrahedral configuration (d_{CH} = = 0.1093 nm, $\mu = 0$) that corresponds to the following electron configuration:

$$[\sigma_s]^2[\sigma_x]^2[\sigma_y]^2[\sigma_z]^2$$

Methane is a colourless, odourless gas (m.p. —182.48 °C, b.p. —161.49 °C), chemically inert because of the valence and coordination saturation of its molecule. It does not react with acids or alkalis, but it burns easily and its mixtures with air are very explosive. Methane is the principal constituent of natural gas (60-90 per cent), fire damp, and marsh gas. It occurs in the Earth's crust in the form of clathrates (see p. 268). Methane is formed in large quantities during the coking of coals. Gases rich in it are used as high-calorific fuels and as raw materials for the manufacture of water gas (see p. 280).

Carbon forms many *percarbides* which are more varied than peroxides or pernitrides because of the high strength of carbon homochains. Certain very simple hydrocarbons, isoelectronic analogues of peroxide and pernitride of hydrogen can be formally regarded as the simplest percarbides:

Peroxide	Pernitride	Percarbide	Hybridisation of atomic orbitals (O, N, C)
			sp^3
Hydrogen peroxide	Hydrazine	Ethane	
			sp^2
	Diimide	Ethylene	
			sp
		Acetylene	

In normal conditions *ethane* C_2H_6, *ethylene* C_2H_4, and *acetylene* C_2H_2 are gases. Because of the great strength of the bond, C_2H_6 (E_{CC} = 347 kJ/mol), C_2H_4 (E_{CC} = 598 kJ/mol), and C_2H_2 (E_{CC} = 811 kJ/mol) are quite stable (in contrast to H_2O_2, N_2H_4, and especially N_2H_2) and of low chemical activity.

The internuclear distances d_{CC} with single, double, and triple bonds between carbon atoms are 0.154, 0.135 and 0.120 nm while the force constants k_{CC} are 450, 960 and 156 N/m respectively. Depending on the type of hybridisa-

tion of the valence orbitals of the carbon atoms, the CH bond length is 0.1093 nm (sp^3 hybridisation), 0.1071 nm (sp^2 hybridisation), and 0.1057 nm (sp hybridisation). The internuclear distance in the C_2^{2-} ion is 0.119 to 0.124 nm.

Ionic-covalent carbides are crystalline, salt-like solids. They are decomposed by water or dilute acid with liberation of hydrocarbons. Carbides of this type can therefore be regarded as derivatives of the corresponding hydrocarbons.

The carbides Be_2C (m.p.. 2150 °C) and Al_4C_3 (m.p. 2800 °C) can be regarded as derivatives of methane, or *methanides*. They are high-melting crystalline solids. According to X-ray crystallography, the carbon atoms are not connected with one another in their crystals. Methanides are decomposed by water, liberating methane:

$$Al_4C_3\ (c) + 12H_2O\ (l) = 4Al(OH)_3\ (c) + 3CH_4\ (g)$$
$$\Delta G^\circ_{298} = -1770\ \text{kJ}$$

Acetylides of the type $\overset{+1}{M}_2C_2$, $\overset{+2}{M}C_2$ and $\overset{+3}{M}_2(C_2)_3$ are relatively the best studied salt-like percarbides. Acetylides are more characteristic of Group I and II *s* and *d* elements and of aluminium.

They are formed by exchange reactions in solutions

$$2AgNO_3 + H_2C_2 = Ag_2C_2\downarrow + 2HNO_3$$

or by direct interaction by heating C_2H_2 with certain metals:

$$2Al + 3H_2C_2 = Al_2(C_2)_3 + 3H_2$$
$$Zn + H_2C_2 = ZnC_2 + H_2$$

Calcium acetylide CaC_2, usually called *calcium carbide*, a very important product, is obtained by heating CaO with carbon in electric furnaces:

$$CaO + 3C = CaC_2 + CO, \qquad \Delta H^\circ_{298} = 462\ \text{kJ}$$
$$\Delta S^\circ_{298} = 228\ \text{J/K}$$

Acetylides are more or less easily decomposed by water

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

with the formation of acetylene. The derivatives of Group I *s* elements are explosive, and acetylides of Group I and II *d* elements (Cu_2C_2, Ag_2C_2, Au_2C_2, HgC_2) are extremely explosive even in the dry state. Calcium acetylide CaC_2 is widely used as a source of acetylene.

The capacity to form compounds with delocalised bonds, up to metallic ones, increases in the F—O—N—C series. Carbides of Group IV, V, VI, VII, and VIII *d* elements are metallic compounds. They are inclusion compounds, i.e. the carbon atoms occupy octahedral cavities in the close-packed structures of the metal atoms. Metal carbides are most varied, the commonest are those with an

average MC composition (TiC, ZrC, HfC, VC, NbC, TaC), M_2C composition (Mo_2C, W_2C), or M_3C composition (Mn_3C, Fe_3C, Co_3C). These carbides have such metallic properties as metallic lustre, high electrical conductivity (which decreases with rising temperature) and the readiness with which they form solid solutions with metals, and so on. The composition of *d* element carbides varies within wide limits; for example, the carbides of titanium and vanadium, depending on the conditions, may have a $TiC_{0.6-1.0}$ and $VC_{0.58-1.0}$ composition.

The carbides of *d* elements are very hard refractory materials usually melting at higher temperatures than the initial metals; for example,

Metal	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Mn	Fe
M. p., °C	1668	1852	2200	1919	2460	3000	2620	3380	1244	1539

Carbide	TiC	ZrC	HfC	VC	NbC	TaC	Mo_2C	W_2C	Mn_3C	Fe_3C
M. p., °C	3150	3580	3670	2800	3500	3880	2690	2800	1520	1650

Carbides with an MC composition (TiC, VC, NbC) and M_2C composition (Mo_2C, W_2C), in addition to their extremely high refractoriness (melting at temperatures above 2000 °C to 3500 °C), are also highly resistant to corrosion.

Carbides with an M_3C composition (Mn_3C, Fe_3C, Co_3C) are less stable both thermally and chemically, and are decomposed by dilute acids with liberation of a mixture of hydrocarbons.

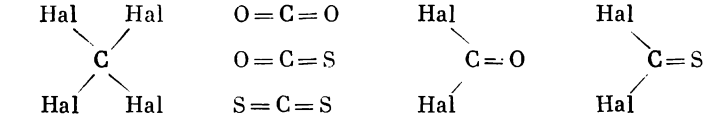
Carbides are prepared by calcining mixtures of powdered metals or their oxides with carbon at high temperatures in electric furnaces:

$$V_2O_5 + 7C = 2VC + 5CO$$

Metal carbides are constituents of pig iron and steels, and lend them hardness, resistance to wear, and other valuable properties. Carbides of tungsten, titanium, and tantalum are employed to produce extra-hard refractory alloys for high-speed machining of metals. They are obtained by the techniques of powder metallurgy (pressing constituents on heating), generally employing cobalt and nickel as cementing agents. An alloy of 20 per cent HfC and 80 per cent TaC is the most refractory of all substances known (m.p. 4400 °C).

Compounds of carbon(IV). An oxidation state of carbon + 4 is observed in compounds with nonmetals that are more electronegative than carbon itself: $CHal_4$, CO_2, CS_2, $COHal_2$ and $CSHal_2$. Depending on the hybrid state of the carbon valence orbitals, the molecules of its halides $CHal_4$ are tetrahedral, of the oxide CO_2 and sulphide CS_2 linear, while the oxyhalides and sulphide halides $COHal_2$ and

$CSHal_2$ have triangular structures:



sp^3 Hybridisation of carbon orbitals — *sp* Hybridisation of carbon orbitals — sp^2 Hybridisation of carbon orbitals

In normal conditions, some of these are gases (CF_4, CO_2, COS, $COCl_2$), while others are liquids (CCl_4, CS_2) or low-melting solids (CBr_4, CI_4). In the solid state all have molecular lattices.

These compounds of carbon(IV) are acidic in nature, and some quite readily react with water to form acids

$$CO_2 + H_2O = H_2CO_3$$

$$COCl_2 + 2H_2O = H_2CO_3 + 2HCl$$

and with basic compounds to form salts

$$2KOH + CO_2 = K_2CO_3 + H_2O$$

$$2KNH_2 + CO_2 = K_2CN_2 + 2H_2O \text{ (in liquid } H_3N)$$

$$CaS + CS_2 = CaCS_3$$

$$Ca_3N_2 + C_3N_4 = 3CaCN_2 \text{ (in liquid } H_3N)$$

Selected constants of carbon *tetrahalides* are listed in the following table:

	CF_4	CCl_4	CBr_4	CI_4
M. p., °C	—184	—23	94	171 (decomposes)
B. p., °C	—128	77	187	sublimes
d_{CHal}, nm	0.136	0.176	0.194	0.215
E_{CHal}, kJ/mol	487	340	285	214
$\Delta H^\circ_{f,\,298}$, kJ/mol	—634	—103	79	—
$\Delta G^\circ_{f,\,298}$, kJ/mol	—888	—61	67	261

In normal conditions CF_4 is a gas, CCl_4 a liquid, and CBr_4 and CI_4 solids. The first two are colourless, CBr_4 is pale yellow, and CI_4 pale red. All are practically insoluble in water and are soluble only in organic solvents. Carbon tetrafluoride is very resistant to heat and chemical reagents; the tetrachloride is less stable, but does not decompose by either acids or alkalis. It is hydrolysed only at high temperature in the presence of catalysts (metals). The variation of the Gibbs' energy in the reaction

$$CHal_4\,(g) + 2H_2O\,(g) = CO_2\,(g) + 4HHal\,(g)$$

indicates a thermodynamic probability of hydrolysis of CF_4 (ΔG°_{298} = —150 kJ/mol) and CCl_4 (ΔG°_{298} = —250 kJ/mol). Its absence in normal conditions is due to the kinetic factor: a coordination-saturated carbon atom does not tend to unite with water molecules

(i.e. to accept electron pairs from H_2O molecules in order to initiate hydrolysis).

As bond length C—Hal increases and bond strength decreases in the CF_4—CCl_4—CBr_4—CI_4 series, the compounds become less stable and their chemical activity increases.

Carbon tetrafluoride can be obtained either by direct interaction of the simple substances or by an exchange reaction between CCl_4 and AgF at 300 °C. The tetrachloride is prepared by chlorination of CS_2 in the presence of a catalyst:

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2$$

Carbon tetrachloride CCl_4 is the most important tetrahalide of carbon and is widely used as a noncombustible solvent of organic substances. It is also used as fire-extinguishing liquid. A mixed fluoride-chloride of carbon CCl_2F_2, commonly known as *freon* (f.p. —30 °C) is used as a refrigerant.

The molecule of *carbon dioxide* CO_2 has a linear configuration (d_{CO} = 0.1162 nm, $\mu = 0$), which corresponds to the electron configuration

$$[2s_a]^2[2s_b]^2[\sigma_s]^2[\sigma_z]^2[\pi_{x,\,y}]^4[\pi^{non}_{x,\,y}]^1$$

In other words, its bonds are realised through four electron pairs in four three-centre orbitals. In the theory of localised bonds, this corresponds to an arrangement of four electron pairs in four two-centre orbitals

$$:\ddot{O}=C=\ddot{O}:$$

two of which (σ type) arise through the overlapping of two *sp* hybrid orbitals of C and two $2p_z$ orbitals of O. Two other π type localised orbitals arise through overlapping of the $2p_x$ and $2p_y$ orbitals of carbon and the $2p_x$ and $2p_y$ oxygen orbitals. The role of the oxygen atoms' unshared electron pairs is performed by nonbonding $2s_a$, $2s_b$ and $\pi_{x,y}$ electrons.

For the reaction

$$C\ (graphite) + O_2\ (g) = CO_2\ (g)$$

the entropy change is insignificant ($\Delta S \simeq 0$), so that the Gibbs' energy change depends substantially on the enthalpy change, i.e. $\Delta H \cong \Delta G$. The heat of this reaction can consequently be almost completely used to perform work (see p. 229), which could be achieved if the reaction were realised in a fuel cell. When the reaction of burning coal is used in a furnace—steam boiler—turbine—electrical generator system, the efficiency of the reaction is only 20 to 30 per cent.

Carbon dioxide (sublimes at —78.5 °C, m.p. —56.5 °C at $5 \times 10_5$ Pa) is obtained industrially by thermal decomposition of $CaCO_3$ and in the laboratory by the action of hydrochloric acid on $CaCO_3$.

The solubility of CO_2 in water is low (at 0 °C 1.7 litre of CO_2 per litre of water and at 15 °C 1 litre). Some of the dissolved carbon dioxide reacts with the water to form carbonic acid H_2CO_3. Carbon dioxide is readily absorbed in alkali solutions with formation of a corresponding carbonate or hydrocarbonate (with an excess of CO_2):

$$2OH^- + CO_2 = CO_3^{2-} + H_2O, \quad OH^- + CO_2 = HCO_3^-$$

Carbon dioxide is used in the manufacture of soda, as a fire extinguisher, to make carbonated beverages, and as an inert medium for various types of synthesis.

Carbon disulphide CS_2 is a volatile colourless liquid in normal conditions (m.p., —111.6 °C, b.p., —46.3 °C). It is prepared by the interaction of sulphur vapour and incandescent coal. Carbon disulphide is an endothermic compound (ΔH_f° = 122 kJ/mol); it is easily oxidised, and ignites in air when slightly heated

$$CS_2 + 3O_2 = CO_2 + 2SO_2$$

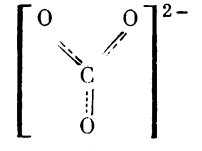
It is insoluble in water, but when heated (at 150 °C) is hydrolysed into CO_2 and H_2S. It is employed as a good solvent of organic compounds, phosphorus, sulphur, and iodine. The bulk of CS_2 is used in the manufacture of viscose rayon and to control agricultural pests. *Carbon disulphide is poisonous!*

Oxydihalides of carbon(IV), COF_2, $COCl_2$ and $COBr_2$, are known. Their molecules are planar triangles. Since the bonds are not equivalent, the $COHal_2$ molecules are polar.

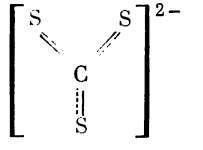
	COF_2	$COCl_2$	$COBr_2$
M. p., °C	—114	—118	—
B. p., °C	—83	+8	+65
d_{CHal}, nm	0.131	0.175	—
d_{CO}, nm	0.117	0.117	—
$\mu_{COHal_2} \times 10^{29}$, C·m	32	39	—

All the oxydihalides (carbonyl halides) are much more reactive than the tetrahalides; in particular, they are readily hydrolysed. *Phosgene* or *carbonyl chloride* ($COCl_2$) is widely used in organic synthesis. It is an extremely *poisonous gas.*

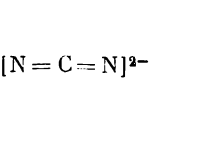
The simplest anion complexes of carbon(IV) (*carbonates*) are CO_3^{2-}, CS_3^{2-} and CN_2^{2-}:



Trioxycarbonate ion (sp^2 hybridisation of the carbon atom)



Trisulphide carbonate ion (sp^2 hybridisation of the carbon atom)



Dinitride carbonate ion (sp hybridisation of the carbon atom)

Oxycarbonates are prepared by the interaction of CO_2 and alkali solutions, or by exchange reactions. Carbonates of sodium and elements of the potassium subgroup are soluble only in water. The action of CO_2 on carbonates in the presence of water yields hydrocarbonates:

$$CaCO_3\ (s) + CO_2\ (g) + H_2O\ (l) \rightleftharpoons Ca(HCO_3)_2\ (sol)$$

The hydrocarbonates in contrast to the carbonates are soluble, as a rule, in water.

Hydrogen trioxycarbonate H_2CO_3 is known only in dilute aqueous solution (*carbonic acid*); it is formed by the interaction of CO_2 and water. Most of the dissolved CO_2 is in its hydrated form $CO_2 \cdot aq$ and only some in the form of H_2CO_3, HCO_3^-, and CO_3^{2-}.

Carbonic acid is an acid of medium strength ($K_{a_1} = 1.3 \times 10^{-4}$, $K_{a_2} = 5.0 \times 10^{-11}$.)

Sulphide carbonates(IV) (thiocarbonates) resemble trioxycarbonates(IV) in many respects. They can be obtained by the interaction of carbon disulphide and basic sulphides; for example,

$$K_2S + CS_2 = K_2[CS_3]$$

Hydrogen trisulphide carbonate H_2CS_3 is an oily liquid (m.p., —31 °C) formed by the action of hydrochloric or sulphuric acid on corresponding thiocarbonates:

$$K_2CS_3 + 2HCl = H_2CS_3 + 2KCl$$

The aqueous solution of H_2CS_3 is weak thiocarbonic acid, which decomposes gradually in water forming carbonic acid and hydrogen sulphide:

$$H_2CS_3 + 3H_2O = H_2CO_3 + 3H_2S$$

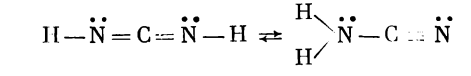
Mixed oxysulphide carbonates, derivatives of $[COS_2]^{2-}$ and $[CO_2S]^{2-}$ complexes are also known.

$CaCN_2$, known as *calcium cyanamide*, is an important nitride carbonate. It is prepared by oxidising calcium carbide CaC_2 by nitrogen over heat:

$$CaC_2 + N_2 = CaCN_2 + C$$

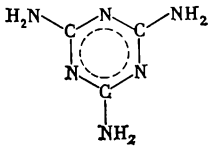
Calcium cyanamide is used as a fertilizer and in the manufacture of ammonia and certain nitrous derivatives of carbon.

Hydrogen dinitride carbonate H_2CN_2 (*cyanamide*) is a colourless, crystalline solid (m.p., +46 °C), readily soluble in water, alcohol, and ether. It exhibits weak acidic properties. In organic solvents, there is probably equilibrium of tautomeric forms:

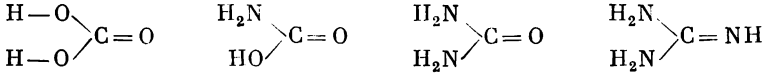


Water decomposes H_2CN_2 gradually into carbonic acid and ammonia.

Liquid cyanamide is polymerised into trimeric ring molecules of melamine



The structural formulas of the nitride and oxynitride carbonates of hydrogen, which can be regarded as derivatives of H_2CO_3 in which the OH^- and O^{2-} are displaced by NH_2^- and NH^{2-} radicals, are as follows:



Carbonic acid — Carbamic acid — Urea — Guanidine

The most important of these compounds is *urea* $CO(NH_2)_2$ (*carbamide*), a white crystalline solid (m.p., 132.7 °C), obtained by the action of CO_2 on an aqueous solution of H_3N at 130 °C and a pressure of 1×10^7 Pa:

$$CO_2 + 2H_3N = CO(NH_2)_2 + H_2O$$

It is used as a fertilizer and in animal feeds. This is also the primary product for making various plastics, pharmaceuticals (veronal, Luminal), etc.

In addition to CN_2^{2-}, the CON^- and CSN^- anions also correspond to the *sp* hybrid state of carbon

$$[N{=}C{=}N]^{2-} \qquad [O{=}C{=}N]^- \qquad [S{=}C{=}N]^-$$

The derivatives of CNO^- and CNS^- are known respectively as *cyanates* and *thiocyanates*. In an aqueous solution, hydrogen oxynitride carbonate HCNO (*cyanic acid*, $K = 1.2 \times 10^{-4}$) exists in tautomeric forms:

$$H{-}O{-}C{\equiv}\ddot{N} \rightleftarrows O{=}C{=}\ddot{N}{-}H$$

Many nitride and oxynitride carbonates decompose gradually in water, liberating ammonia

$$KCNO + 2H_2O = KHCO_3 + H_3N$$

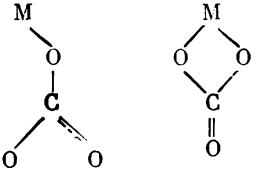
$$CaCN_2 + 3H_2O\ (\text{steam}) = CaCO_3 + 2H_3N$$

The second reaction is used to obtain ammonia by the cyanamide method.

Hydrogen sulphide nitride carbonate(IV) HSCN (*hydrogen thiocyanate*, H—S—C≡N—) is a colourless, very unstable oily liquid (m.p., 5 °C) miscible with water in any proportion to form a strong thiocyanic acid ($K = 0.14$) (of the HCl type). Thiocyanates are used mainly for dying textiles; NH_4CNS is used as a reagent for Fe^{3+}.

Carbonate(IV) complexes, in particular CNO^- and CNS^-, can act as ligands in complex compounds, e.g. $K_3[Fe(CNS)_6]$ and $Na_2[Ni(CNO)_4]$.

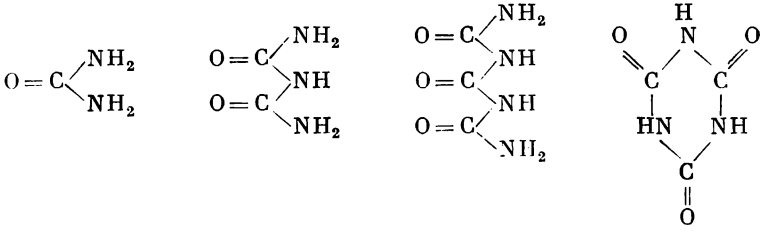
The CNS^- and CNO^- ions are monodentate ligands, while the CO_3^{2-} ion can act as both a monodentate and bidentate ligand



Monodentate Bidentate

e.g. in $[Co(NH_3)_5CO_3]Br$ and $[Co(NH_3)_4CO_3]Br$

Numerous *heterochain* compounds are known for carbon(IV), e.g.

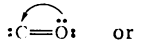


Urea Biuret Triuret Cyanuric acid

They are crystalline solids used mainly in organic synthesis.

Compounds of carbon(II). The derivatives of carbon(II) are CO, CS, and HCN. The molecule of carbon(II) *oxide* CO has a triple bond like the molecule N_2, which is isoelectronic to it. According to valence bond theory, two bonds are formed by pairing $2p$ electrons of the C and O atoms,

and the third bond through a donor-acceptor mechanism (involving a free $2p$ carbon orbital and $2p$ electron pair of oxygen):

 or $C \equiv O$

According to the molecular orbital theory, this corresponds to the following electron configuration of the CO molecule in the ground state (see Table 40):

$$[\sigma_s]^2[\sigma_s^*]^2[\pi_{x,\,y}]^4[\sigma_z]^2$$

This configuration can be interpreted as follows. Two occupied σ_s orbitals correspond to two electron pairs (one predominantly localised at the carbon atom and the other at the nitrogen atom). An occupied σ_z orbital corresponds to σ bond between the carbon and oxy-

Table 40. **Distribution of Electrons in the Orbitals of CO Molecule and CN^- Ion**

Molecular orbitals	CO [C ≡ O]	CN^- [C ≡ N]$^-$
σ_z^*	—	—
$\pi_x^*\pi_y^*$	— —	— —
σ_z	↑↓	↑↓
$\pi_x\pi_y$	↑↓ ↑↓	↑↓ ↑↓
σ_s^*	↑↓	↑↓
σ_s	↑↓	↑↓
Internuclear distance, nm	0.1128	0.114
Dissociation energy, kJ/mol	1069	945

gen atoms. An occupied doubly degenerate π level corresponds to two π bonds. The CO molecule has very high dissociation energy (1069 kJ/mol), a high force constant (k_{CO} = 1860 N/m), and a short internuclear distance (0.1128 nm). Its dipole moment is insignificant ($\mu = 0.04 \times 10^{-29}$ C·m), the effective charge on the carbon atom being negative and on the oxygen atom positive.

Since the structure of the CO and N_2 molecules is similar their physical properties are also alike; both melt and boil at very low temperatures (for CO these points are —204 °C and —191.5 °C respectively); their standard entropies are similar (for CO 197.5 J/K·mol, for N_2 199.9 J/K·mol); in the solid state, both carbon monoxide and diatomic nitrogen exist in two forms (cubic and hexagonal); both are only barely soluble in water, and so on. Their similarity is also exhibited in the structure of their spectra.

Carbon(II) oxide is formed when carbon or its compounds are burned in insufficient oxygen, and also by the interaction of carbon(IV) oxide and coal when heated:

$$CO_2\,(g) + C\,(c) \rightleftarrows 2CO\,(g), \quad \Delta H = 120\ kJ, \quad \Delta S = 176\ J/K$$

The reaction is reversible. It proceeds to the right under the entropy factor and to the left under the enthalpy factor. Equilibrium is displaced in practice at temperatures below 400 °C toward the formation of CO_2, and at temperatures above 1000 °C toward the formation

of CO (Fig. 171). Its velocity at low temperatures is insignificant; in normal conditions carbon(II) oxide does not undergo disproportionation, i.e. is quite stable.

Carbon(II) oxide is normally chemically inert. When heated it exhibits reducing properties, which are widely used in pyrometallurgy (see p. 249). At 700 °C it burns in air with a blue flame, generating much heat (283 kJ/mol):

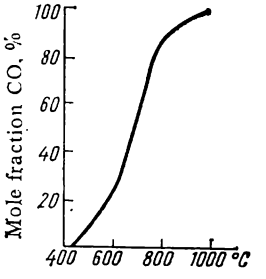


Fig. 171. Effect of temperature on the equilibrium of $CO_2(g) + C(c) = 2CO(g)$

$$CO\ (g) + 1/2O_2\ (g) = CO_2\ (g).$$
$$\Delta G^\circ_{298} = -257\ \text{kJ}$$
$$\Delta S^\circ_{298} = -86\ \text{J/K}$$

It is oxidised by sulphur when heated:

$$CO\ (g) + S\ (g) = COS\ (g),$$
$$\Delta G^\circ_{298} = -229\ \text{kJ}$$
$$\Delta S^\circ_{298} = -134\ \text{J/K}$$

Under radiation or in the presence of a catalyst, CO reacts with chlorine to form oxychloride $COCl_2$.

The CO molecule can act as a ligand in various complexes. The nonbonding electron pair of the carbon atom accounts for its σ donating properties while the free π^* orbitals account for its π accepting properties (see Fig. 228).

The cyanide ion CN^-, which is isoelectronic with the CO molecule, has a similar structure (see Table 40). Its electron configuration in the ground state

$$[\sigma_s]^2[\sigma_s^*]^2[\pi_{x,\,y}]^4[\sigma_z]^2$$

can be interpreted in the same way as that of the CO molecule. Two occupied σ_s orbitals correspond to two electron pairs, one predominantly localised at the nitrogen atom, and the other at the carbon atom. The occupied σ_z orbital corresponds to a σ bond, while the four electrons in the doubly degenerate π level correspond to two π bonds between the C and N atoms:

$$[:C{\equiv}N:]^-$$

Cyanides may be acidic or basic in chemical nature. During hydrolysis, the ionic cyanide NaCN, for instance, forms an alkaline medium, while the covalent ICN forms two acids:

$$\underset{\text{Basic}}{NaCN + HOH \rightleftarrows NaOH + HCN}, \qquad \underset{\text{Acidic}}{ICN + HOH = HIO + HCN}$$

The cyanides of *d* elements are not soluble in water but are readily so in the presence of basic cyanides (through the formation of complexes):

$$4KCN + Fe(CN)_2 = K_4[Fe(CN)_6]$$

The *hydrogen cyanide* molecule HCN has a linear structure (d_{CH} = = 0.106 nm, d_{CN} = 0.116 nm):

$$\overset{0.04+}{H} - \overset{0.17+}{C} \equiv \overset{0.21-}{N}$$

There is also a tautomeric form (*hydrogen isocyanide*)

$$\overset{0.04+}{H} - \overset{0.75+}{N} \rightleftarrows \overset{0.71-}{C}$$

The first isomer is more stable because the effective charges on the atoms are lower than in the second.

The molecules of HCN are highly polar ($\mu = 0.9 \times 10^{-29}$ C·m), because of the hydrogen bond they associate into colourless liquid (m.p. —13.3 °C, b.p. 25.7 °C). Hydrogen cyanide mixes with water in any proportion. The aqueous solution is a very weak acid (K_a = = 7.9×10^{-10}) known as *prussic* or *hydrocyanic acid.*

Hydrogen cyanide is an endothermic compound ($\Delta H_f^\circ = 109$ kJ/mol, $\Delta G_f^\circ = 126$ kJ/mol). Liquid HCN is gradually polymerised.

Being derivatives of carbon(II), cyanides have reducing properties; so when their solutions are heated, they are gradually oxidised by atmospheric oxygen to form cyanates

$$2\overset{+2}{C}N^- + O_2 = 2\overset{+4}{C}NO^-$$

while boiling them with sulphur results in thiocyanates

$$\overset{+2}{C}N^- + S = \overset{+4}{C}NS^-$$

The last reaction is the one used to obtain thiocyanates. Cyanides are obtained by reducing carbonates(IV) by carbon with heating

$$Na_2\overset{+4}{C}O_3 + \overset{0}{C} + 2H_3N = 2Na\overset{+2}{C}N + 3H_2O$$

$$Ca\overset{+4}{C}N_2 + \overset{0}{C} + Na_2CO_3 = CaCO_3 + 2Na\overset{+2}{C}N$$

and by reactions not associated with oxidation-reduction of the elements. HCN, for example, is produced industrially by heating a mixture of CO and H_3N under pressure in the presence of a catalyst (ThO_2):

$$CO + H_2NH = HCN + H_2O$$

Hydrogen cyanide is used in organic synthesis, and NaCN and KCN are used in the recovery of gold, to obtain complex cyanides, and so on. *Cyanides are extremely poisonous*!

When the cyanides of inactive metals, e.g. AgCN, $Hg(CN)_2$, are heated to between 350 °C and 450 °C, *cyanogen* (*dicyan*) $(CN)_2$ is formed

$$Hg(CN)_2 = Hg + (CN)_2$$

It is a very reactive poisonous gas (m.p. —34.4 °C, b.p. —21.2 °C). Its properties (d_{CC} = 0.137 nm, d_{CN} = 0.113 nm) correspond to the following structure

$$:N \equiv C-C \equiv N:$$

The Gibbs' free energy of its formation has a high positive value (ΔG_f° = 309.2 kJ/mol), so that it cannot be synthesised from the simple substances. For the same reason it is readily oxidised by oxygen to give a very hot flame (approximately 4780 °C). Cyanogen can be regarded as a pseudohalogen since it behaves like a halogen in certain reactions; in its reaction with hydrogen, for example, gaseous HCN is formed

$$(CN)_2 + H_2 = 2HCN$$

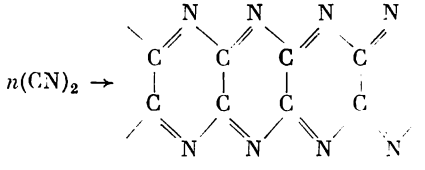
which (like HHal) behaves like an acid in an aqueous solution. Like the halogens, too, cyanogen undergoes disproportionation in alkaline solutions:

$$(CN)_2 + 2OH^- = CN^- + CNO^- + H_2O$$

It can also act as a reducing agent:

$$(CN)_2 + Cl_2 = 2CNCl$$

Pure cyanogen is stable, but it polymerises when heated:



Cyanogen chloride CNCl is a gas in normal conditions (m.p. —6 °C, b.p. 13.8 °C). It is a covalent compound, acidic in chemical nature, reacting with alkalis to give cyanate and chloride ions:

$$CNCl + 2OH^- = CNO^- + Cl^- + H_2O$$

6.2. Silicon

Silicon Si ($1s^2 2s^2 2p^6 3s^2 3p^2$) is an analogue of carbon as regards the number of valence electrons, but its atom is larger, its ionisation energy lower, and its electron affinity and polarisability higher. Therefore, as an element of the third period, it differs substantially from carbon, an element of the second period, in structure and properties. Its maximum coordination number is six and most characteristic number four. Like the other elements of the third period, $p\pi$ — $p\pi$ bonding is not characteristic of silicon, so that, in contrast to carbon, its *sp* and sp^2 hybrid states are unstable. In compounds silicon exhibits +4 and —4 oxidation states.

From another angle the difference in the properties of silicon and carbon is due to the presence of vacant 3*d* orbitals in the silicon atom.

The bond energies of silicon and carbon with selected elements are given in Table 41. Si—F and Si—O bonds are most characteristic of silicon; for that reason it occurs in the crust especially in its oxygen compounds.

Natural silicon has three stable isotopes: ^{28}Si (92.27 per cent), ^{29}Si (4.68 per cent) and ^{30}Si (3.05 per cent).

Silicon is second only to oxygen in abundance (20 mole per cent). About half the Earth's crust consists of silica SiO_2 and silicate and aluminosilicate rocks.

The simple substance. In accordance with its characteristic type of hybridisation (sp^3) of valence orbitals, the most stable form of silicon is a diamond-like (cubic) one. Like diamond, this form is refractory (m.p., 1412 °C) and extremely hard. Because of partial delocalisation of the bond, it has a dark grey colour, metallic appearance and is a semiconductor at room temperature ($\Delta E = 1.12$ eV). The hexagonal (graphite-like) modification is unstable.

Table 41. **Bond Energies of SiX and CX**

Bond	Energy, kJ/mol	Bond	Energy, kJ/mol
SiO	445	CI	214
CO	359	SiN	330-350
SiF	567	CN	206
CF	487	SiH	319
SiCl	382	CH	414
CCl	340	SiSi	222
SiBr	310	CC	348
CBr	285	SiC	328
SiI	235		

In normal conditions silicon is quite inert. It reacts with simple substances (except fluorine) only at elevated temperatures, generally exhibiting reducing properties. Thus, it is oxidised by chlorine at 400 °C and by oxygen at 600 °C. It reacts with nitrogen only at 1000 °C (forming Si_3N_4) and with carbon at 2000 °C (forming SiC).

Silicon is passivated in oxyacids and is only soluble in a mixture of hydrofluoric and nitric acids

$$\overset{0}{3Si} + 4\overset{+5}{H}NO_3 + 18HF = 3\overset{+4}{H_2}SiF_6 + 4\overset{+2}{N}O + 8H_2O$$

In this reaction HNO_3 acts as an oxidant and HF as a complex-forming medium; in it silicon passes into its stable +4 oxidation state and becomes part of a stable fluorine complex SiF_6^{2-} (ΔG_f° of the dissolved SiF_6^{2-}, —2133 kJ/mol).

Silicon dissolves vigorously in alkalis with liberation of hydrogen

$$\overset{0}{Si} + \overset{+1}{H_2O} + 2KOH = \overset{+4}{K_2SiO_3} + \overset{0}{2H_2}$$

In this reaction, water acts as an oxidant and the OH^- ion as a complex-forming medium.

In normal conditions silicon does not react with water but at high temperatures the following reaction occurs:

$$Si + 3H_2O\ (g) = H_2SiO_3 + 2H_2\ (g)$$

Silicon's oxidising activity is exhibited only in relation to certain metals, e.g.

$$2Mg + Si = Mg_2Si$$

Technical silicon (95 to 98 per cent pure) is prepared by reducing SiO_2 by coke in electric furnaces. In the laboratory magnesium is used as the reducing agent, which yields a heavily contaminated brown silicon powder. The powder can be converted to the crystalline state by recrystallisation from metallic melts (Zn, Al, etc.). The very pure silicon required for semiconductor devices is obtained by reducing $SiCl_4$ by zinc at high temperatures

$$SiCl_4 + 2Zn = Si + 2ZnCl_2$$

and by thermal decomposition of its hydrogen compounds or SiI_4

$$SiH_4 = Si + 2H_2, \quad SiI_4 = Si + 2I_2$$

It is further purified by zone refining.

Monocrystals of silicon containing certain additives are used in the manufacture of various semiconductor instruments (rectifiers, photo cells, etc.). Silicon photo cells (converters of light into electricity) are used in spacecraft to supply power for radio instruments.

In addition to its use as a semiconductor, silicon is widely employed in the steel industry to kill (deoxidise) steels and make them more corrosion resistant. An alloy of silicon and iron (*ferrosilicon*), obtained by joint reduction of iron ore and silica by coke, is used for this purpose. Ferrosilicon is very resistant to the action of acids and so is widely used in the manufacture of acid-resistant articles.

Compounds of silicon with a negative oxidation state. During the oxidation of metals by silicon (700 °C to 1200 °C), or heating of a mixture of their oxides and silicon in an inert medium, *silicides* are formed:

$$2Mg + Si = Mg_2Si$$
$$6MnO + 5Si = 2Mn_3Si + 3SiO_2$$

They differ in structure and properties from carbides.

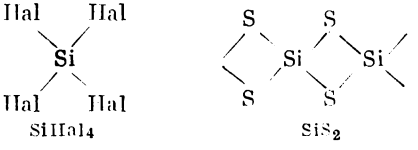
Depending on the type of elements that are less electronegative than silicon itself, the type of bond in silicides changes from ionic-covalent to metallic. Silicides of Group I and II *s* and *d* elements, e.g. Ca_2Si, CaSi, and $CaSi_2$, are semiconductors. Silicides of this type are chemically unstable, and are more or less readily decomposed by water, and especially by acids.

The silicides of *d* and *f* elements generally have a complicated composition (e.g. Mo_3Si, Mo_5Si_3, MoSi, $MoSi_2$) that often does not correspond to the whole oxidation states of the elements involved. Depending on the type of prevailing bond these silicides may be metallic and semiconductors. Silicides containing much silicon are quite resistant to acids and oxidation at high temperatures; $MoSi_2$, for example, is insoluble in all acids (HF and aqua regia included), and is soluble only in a solution of alkalis or a mixture of HF and HNO_3. Most silicides of *d* (*f*) elements are very hard; some melt at high temperatures: for example:

	Ti_5Si_3	V_5Si_3	$MoSi_2$	WSi_2
M. p., °C	2120	2150	2050	2165

Silicides are used in the manufacture of refractory and acid-resistant alloys and as temperature-resistant semiconductors. Molybdenum disilicide $MoSi_2$ can withstand temperatures of 1600 °C to 1700 °C in aggressive media and is therefore used for the heaters in electric furnaces. Several silicides of *f* elements are used as neutron absorbers in nuclear engineering.

Compounds of silicon(IV). Silicon has a +4 oxidation state in its compounds with the halogens, oxygen, sulphur, nitrogen, carbon, and hydrogen. Let us consider some of its binary compounds, viz., $SiHal_4$, SiO_2, SiS_2, Si_3N_4, SiC, and SiH_4. Since the stable coordination number of silicon is four, $SiHal_4$ and SiH_4 are monomers only, while all others are polymers. The unit cell of most Si(IV) compounds is a tetrahedron of more electronegative atoms (SiO_4, SiS_4, SiN_4, SiC_4) with a Si atom at the centre (see, for example, Fig. 70*c*). Schematically the structures of $SiHal_4$ and SiS_2 are as follows:



$SiHal_4$ SiS_2

The polymer compounds with a coordination lattice (SiO_2, SiC) have high melting points and are chemically stable. Monomeric compounds, on the contrary, are low-melting and chemically active. Compounds with a chain structure (SiS_2) occupy an intermediate position.

Anion complexes of silicon(IV) corresponding to the binary compounds (viz., SiO_3^{2-}, SiS_3^{2-}, SiN_2^{2-}), in contrast to the similar compounds of carbon(IV), are polymeric in most cases.

Thus, having the same number of valence electrons, carbon and silicon form compounds of the same composition, but these differ in structure and consequently in chemical activity.

Binary compounds of Si(IV) are chemically acidic; most of them, for instance, interact with alkalis (in solution and especially in melts)

$$SiO_2 + Ca(OH)_2 \xrightarrow{\text{fusion}} CaSiO_3 + H_2O$$

$$SiH_4 + 2KOH + H_2O = K_2SiO_3 + H_2$$

and with other basic compounds

$$CaS + SiS_2 = CaSiS_3$$

They form acids during hydrolysis

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl$$

$$SiS_2 + 3H_2O = H_2SiO_3 + 2H_2S$$

Halides $SiHal_4$ can be obtained by direct interaction of the simple substances. The tetrafluoride is usually obtained by the action of concentrated sulphuric acid on a mixture $SiO_2 + CaF_2$

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

and the tetrachloride by heating a mixture of SiO_2 and carbon in a chlorine atmosphere:

$$SiO_2\,(s) + 2C\,(s) + 2Cl_2\,(g) = SiCl_4\,(g) + 2CO\,(g)$$

$$\Delta H^\circ_{298} = -46.4\ \text{kJ}, \quad \Delta S^\circ_{298} = 226\ \text{J/K}$$

Large quantities of SiF_4 are obtained as by-products in the manufacture of superphosphate.

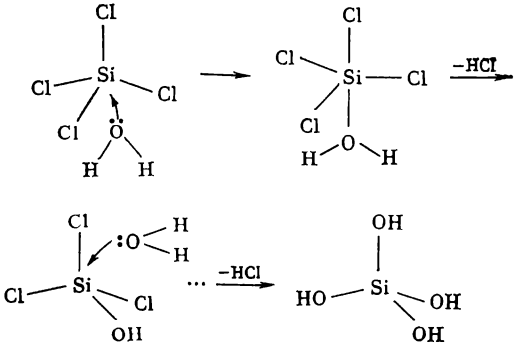
In ordinary conditions SiF_4 is a gas, $SiCl_4$ and $SiBr_4$ liquids, and SiI_4 a solid. All are colourless.

	SiF_4	$SiCl_4$	$SiBr_4$	SiI_4
M. p., °C	—95 (subl.)	—70	5.2	120.5
B. p., °C	—	57.5	152.8	287.5
ΔH°_f, kJ/mol	—1614	—688	—430	—161
ΔG°_f, kJ/mol	—1572	—598	—214	—138
d_{SiHal}, nm	0.155	0.201	0.215	0.243

In contrast to the tetrahalides of carbon, those of silicon are easily hydrolysed, the hydrolysis having an association mechanism (through consecutive attachment of water molecules and elimination of HHal molecules, until the formation of $Si(OH)_4$). Thus the hydrolysis of $SiCl_4$

$$SiCl_4\,(l) + 3H_2O\,(l) = H_2SiO_3\,(s) + 4HCl\,(sol), \quad \Delta G^\circ_{298} = -238\ \text{kJ}$$

can be represented as follows:



The H_4SiO_4 molecules are then polymerised to form a compound with a conventional H_2SiO_3 composition. Silicon tetrahalides fume in humid air, because of hydrolysis.

The increase of the coordination number of silicon(IV) from 4 to 5 in the intermediate compound can be explained by the formation of a three-centre bond. In $SiCl_4 \cdot H_2O$, for instance, three chlorine atoms are linked to the silicon atom by two-centre bonds and one chlorine atom to the water molecule by a three-centre bond.

The acidic nature of SiF_4, unlike that of the other silicon(IV) halides, is not only displayed during hydrolysis but is also manifested in the interaction with basic fluorides, e.g.

$$2KF + SiF_4 = K_2SiF_6$$

Because of the stability of the hexafluorosilicate ion SiF_6^{2-} the hydrolysis of SiF_4 is expressed by the following equations:

$$SiF_4 + 3H_2O = H_2SiO_3 + 4HF$$
$$4HF + 3SiF_4 = 2H_2SiF_6$$

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$$

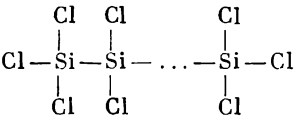
Hydrogen hexafluorosilicate H_2SiF_6 has not been isolated in the free state. Its aqueous solution is a strong acid (of the H_2SO_4 type), known as *hexafluorosilicic acid.*

Fluorosilicates of metals are obtained by the action of hydrofluoric acid on a mixture of silicon and the appropriate fluoride:

$$\overset{+2}{M}F_2 + SiO_2 + 4HF = \overset{+2}{M}SiF_6 + 2H_2O$$

Most are soluble in water. Derivatives of the alkali metals (except lithium) and of barium are only barely soluble. The most important fluorosilicate is Na_2SiF_6, which is used to fluorinate water, as an insecticide, and in the manufacture of acid-resistant cements, enamels, etc. *Silicon tetrafluoride, and all other fluosilicates are poisonous!*

Apart from the monomolecular halides, homochain fluorides and chlorides of the homologous Si_nHal_{2n+1} series have been obtained



and also certain cyclic derivatives. The length of the —Si—Si— homochain does not exceed ten atoms ($Si_{10}H_{22}$). The homochain oligomers of silicon, unlike those of carbon, decompose easily and are active chemically.

Homochains —Si—Si— are found in *hydrides* of silicon (**silanes**) of the Si_nH_{2n+2} homologous series. Silanes are similar in composition (SiH_4, Si_2H_6, Si_3H_8, Si_4H_{10} to Si_6H_{14}) and in physical properties to the corresponding hydrocarbons. In normal conditions the monosilane SiH_4 and disilane Si_2H_6 are gases, the trisilane Si_3H_8 a liquid, and the higher members of the homologous series solids.

	SiH_4	Si_2H_6	Si_3H_8	Si_4H_{10}
M. p., °C	—185	—132	—117	—94
B. p., °C	—112	—15	+53	+86
ΔG_f°, kJ/mol	57	126	—	—

Since Si—H and Si—Si bonds are weaker than C—H and C—C bonds, silanes are much less stable and much more reactive than the corresponding hydrocarbons. Most of them ignite spontaneously in air and generate much heat when burning:

$$SiH_4\ (g) + 2O_2\ (g) = SiO_2\ (c) + 2H_2O\ (g), \quad \Delta H^\circ_{298} = -1357\ kJ$$

Silanes react explosively with the halogens. They are acidic hydrides, as is shown by their reaction with alkalis (see above). They decompose actively even in the presence of traces of alkali, but are quite stable in neutral and acidic media.

Silicon does not interact directly with hydrogen, so that silanes are formed in indirect ways, e.g. by the action of acids on certain silicides:

$$Mg_2Si + 2H_2SO_4 \xrightarrow[\text{in water}]{} SiH_4 + 2MgSO_4$$

$$Mg_2Si + 4NH_4Br \xrightarrow[\text{in liquid ammonia}]{} SiH_4 + 2MgBr_2 + 4H_3N$$

In the second case NH_4Br acts as an acid. The decomposition of silicides by acids in liquid ammonia produces more reaction products than decomposition in an aqueous medium.

Since $p\pi$—$p\pi$ bonds are not characteristic of silicon, hydrides with double and triple bonds between the silicon atoms (analogues of ethylene, acetylene and benzene) are not known.

Silicon *dioxide* SiO_2 (*silica*) has several forms. It occurs in nature mainly as *quartz* (hexagonal structure), but also as *cristobalite* (cubic structure) and *tridymite* (hexagonal structure). The forms of silica differ in the way the SiO_4 tetrahedra are arranged in space.

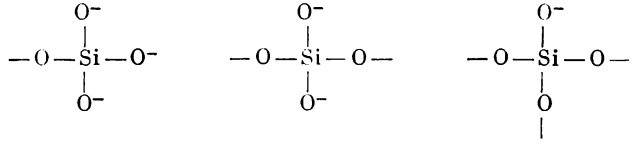
Silica is high melting (1713 °C), very hard, and stable chemically. Only fluorine, hydrofluoric acid, and gaseous HF, phosphoric acid, and alkali solutions react with it. In normal conditions it is insoluble in water but its solubility improves from 150 °C to 0.25 per cent at 500 °C.

Silica is readily vitrified. In contrast to its crystalline modifications, quartz glass has tetrahedral SiO_4 unit cells arranged at random (see Fig. 77). Quartz glass is very stable thermally and chemically and is used in the manufacture of chemical apparatus and optical instruments.

Amorphous silica is also the basis of several minerals, e.g. chalcedony, opal, agate, etc. Quartz sand is used in vast quantities in the manufacture of glass, cement, porcelain, etc.

At ultra-high pressures (approximately 1.2×10^{10} Pa) and temperatures around 1300 °C a special form of SiO_2 is formed, known as *stishovite*, which is 60 per cent denser than quartz. Stishovite has a structure of the rutile type (see Fig. 70*b*), i.e. silicon has the coordination number of six in it. Owing to its close-packed structure, stishovite is even less active than quartz, not reacting even with a concentrated solution of hydrofluoric acid.

The unit cell of *oxysilicates* is a SiO_4 tetrahedron (as in SiO_2). Two neighbouring tetrahedra are linked with one another through one oxygen atom only. Whereas each SiO_4 tetrahedron in SiO_2 (coordination lattice) crystals furnishes four apexes for the forming of Si—O—Si bonds (see Table 10), these tetrahedra can give three, two apexes and even one in oxysilicates:



This explains the great variety of the possible combinations of SiO_4 tetrahedra, and of the structure and types of oxysilicates. In the system $CaO—SiO_2$, for example, the following combinations are possible: Ca_2SiO_4, $Ca_3Si_2O_7$, $CaSiO_3$ (Fig. 172). When an equimolar $CaO + SiO_2$ mixture is heated to between 1000 °C and 1200 °C, Ca_2SiO_4 is first formed, then $Ca_3Si_2O_7$, and finally $CaSiO_3$ (Fig. 173).

The SiO_4 tetrahedra (like PO_4 tetrahedra; see Fig. 160) can unite in pairs ($Si_2O_7^{6-}$), and in closed rings of three ($Si_3O_9^{6-}$), four ($Si_4O_{12}^{8-}$), and six ($Si_6O_{18}^{12-}$) tetrahedra.

Examples of the oxysilicates produced by these unit cells are the minerals *zircon* $Zr[SiO_4]$ and *olivine* $(Mg, Fe)_2[SiO_4]$ (derivatives of the SiO_4^{4-} ion), *thortveitite* $Sc_2[Si_2O_7]$ (a derivative of the $Si_2O_7^{6-}$ ion), *benitoite* $BaTi[Si_3O_9]$, and *wadeite* $K_2Zr[Si_3O_9]$ (derivatives of the $Si_3O_9^{6}$ ion), and *beryl* $Be_2Al_2[Si_6O_{18}]$ (a derivative of the $Si_6O_{18}^{12-}$ ion).

These relatively simple unit cells can, in turn, unite in chains, bands, and networks (Fig. 174). The simplest formula can be calculated from the number of atoms per recurrent link in the polymer structure: SiO_3^{2-}, $Si_4O_{11}^{6-}$, $Si_2O_5^{2-}$

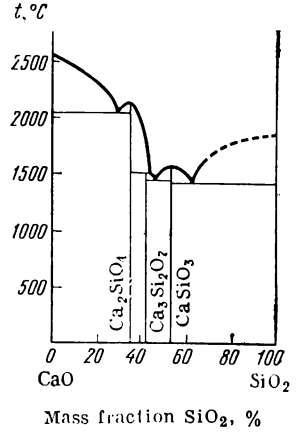


Fig. 172. Phase diagram of a $CaO—SiO_2$ system

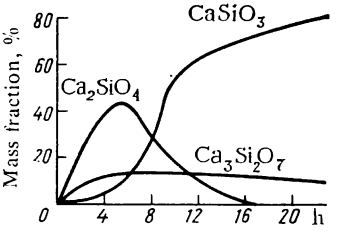


Fig. 173. Formation of intermediate compounds in an equimolar mixture of CaO and SiO_2 at 1000 °C to 1200 °C

The chain oxysilicate anion SiO_3^{2-} includes *pyroxenes*, e.g. *enstatite* $Mg[SiO_3]$, *diopside* $CaMg[SiO_3]_2$, and *spodumene* $LiAl[SiO_3]_2$. Band anions $Si_4O_{11}^{6-}$ include *amphiboles*, of which *tremolite* $Ca_2Mg_5[Si_4O_{11}]_2(OH)_2$ is a typical representative. The oxysilicate sheet anions have a $Si_2O_5^{2-}$ composition.

The chains, bands, and sheets are linked by cations lying between them, and, depending on the type of anion, oxysilicates have a fibrous structure (like *asbestos*) or a sheet one (like *mica*).

Aluminosilicates, as well as silicates, occur widely in nature; AlO_4 tetrahedra are involved along with SiO_4 tetrahedra in the formation of aluminosilicates (see p 457).

Most oxysilicates are insoluble in water; exceptions are silicates of Group I *s* elements. Silicates of sodium and potassium are obtained by boiling SiO_2 in the alkaline solution, which yields a mixture of oxysilicates to which the general formula Na_2SiO_3 or K_2SiO_3 is ascribed.

A concentrated aqueous solution of sodium silicate (*water glass*) is employed in the manufacture of fireproof fabrics, to impregnate wood, as an adhesive, and so on.

A glass-like state is very characteristic of oxysilicates and SiO_2. Common glass is usually made by fusing a mixture of soda (or Na_2SO_4), limestone, and sand, which yields a material with an approximate composition $Na_2O \cdot CaO \cdot 6SiO_2$, consisting of large polymeric anions. Glass is insoluble and inactive chemically. Ordinary glass is given a more or less marked green colour by the iron silicates contained in it.

To get glass with certain physical and chemical properties (transparency, chemical and thermal stability, mechanical strength)-

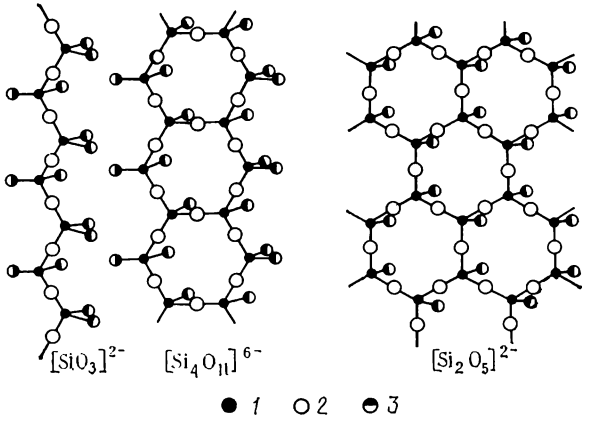


Fig. 174. Polymeric oxysilicate ions:
1 — silicon atom; *2* — oxygen bridge atom; *3* — terminal oxygen atom

appropriate additives are included that alter its composition and structure. If, for example, glass contains potassium instead of sodium (*potassium glass*), its melting (softening) point is higher than that of ordinary *sodium* glass; it is therefore used to make special laboratory apparatus. If lead and potassium replace calcium and sodium, *flint* (or *lead*) *glass* (*crystal glass*) is obtained, with a high refractive index (high density). It is used in the manufacture of high-quality glassware, etc. When cobalt compounds are added, the glass is blue; Cr_2O_3 gives glass emerald green shades, manganese compounds violet tints, and so on; B_2O_3 alter the properties of glass substantially (see p 450).

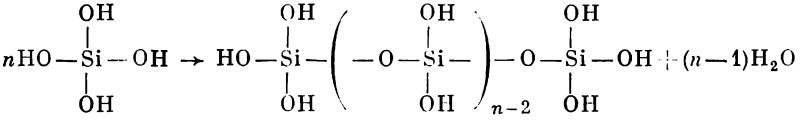
Glass is chemically very stable, but it is very brittle, which is an obstacle to its wide use in the manufacture of tubes and apparatus for the chemical industry. More recently, however, its toughness has been considerably increased by giving it a fine-crystal structure. It is possible, by controlled crystallisation of the molten glass, to obtain *sitals* (*glass ceramics*), homogeneous materials with very fine

crystals, whose strength is sometimes five times that of the initial glass and close to that of cast iron.

Since SiO_2 is practically insoluble in water, silicic acids can only be obtained indirectly, e.g. by the action of acids on solutions of oxysilicates or by hydrolysis of certain Si(IV) compounds (halides, the sulphide, esters of orthosilicic acid, etc.). During the hydrolysis of SiS_2, for example, orthosilicic acid H_4SiO_4 ($K_{a1} = 2 \times 10^{-10}$, $K_{a2} = 2 \times 10^{-12}$) is formed initially:

$$SiS_2 + 4H_2O = H_4SiO_4 + 2H_2S$$

The acid is soluble in water but polymerises more or less rapidly when left to stand:



The middle OH groups can interact in the same way, forming branched and trimeric macromolecules.

The transition from orthosilicic acid to polyacids is accompanied with conversion of the molecular solution of H_4SiO_4 into colloid solutions or *sols*, which in turn either congeal (i.e. turn into *gels*) or yield bulky precipitates of silicic acids containing much water. The composition of the silicic acid obtained largely depends on the initial substances and the reaction conditions.

By heating the precipitates of polysilicic acids finely dispersed SiO_2, or *silica gel*, can be obtained as they gradually dehydrate; silica gel is used as an adsorbent.

Silicon *disulphide* SiS_2 is prepared by fusing amorphous silicon with sulphur in the absence of air or by the following reaction: (at 1300 °C)

$$2H_2S + Si = SiS_2 + 2H_2$$

Silicon disulphide is sublimated *in vacuo* into white fleecy needles (m.p. 1090 °C, b.p. 1130 °C). X-ray crystallography reveals that the needles consist of polymer chains in which the SiS_4 tetrahedra are linked by their edges.

SiS_2 is much more active than SiO_2. It decomposes, for example, in water. When fused with basic sulphides it forms *sulphide silicates* (*thiosilicates*).

Silicon *carbide* SiC (*carborundum*), like carbon and silicon, exists in cubic (diamond-like) and hexagonal forms. In the pure state diamond-like carborundum is an insulator, but with admixtures becomes a semiconductor ($\Delta E = 1.5$-3.5 eV) with *n*- or *p*-conductivity. It is refractory (m.p. 2830 °C) and only exceeded in hardness by diamond. Its chemical stability is high; it is only decomposed

when heated with a mixture of hydrofluoric and nitric acid, and by fusion with alkalis in the presence of oxidants: for example,

$$\overset{-4}{SiC} + 2KOH + 2O_2 = K_2SiO_3 + \overset{+4}{CO_2}$$

Carborundum is prepared in arc furnaces (at 2000 °C to 2200 °C) from a mixture of quartz sand and coke. It is widely used as an abrasive and refractory material; the crystals are used in radio engineering.

Silicon *nitride* Si_3N_4 is very stable chemically and heat resistant. It is a high-melting white powder (subliming at around 1900 °C), very resistant to the action of HF, and solutions of alkalis and metals.

The colourless crystals of Si_3N_4 are semiconductors ($\Delta E = 3.9$ eV). It is used as a chemically stable and refractory material in the manufacture of corrosion-resistant and high-melting alloys, and as high-temperature semiconductor.

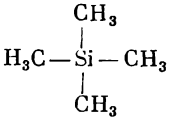
Hydrogen *nitride silicate* H_2SiN_2, unlike H_2CN_2 (*cyanamide*), is a polymer obtained by ammonolysis of $SiCl_4$

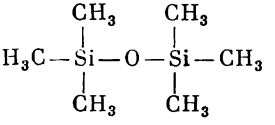
$$SiCl_4 + 6H_3N = H_2SiN_2 + 4NH_4Cl$$

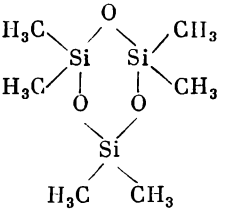
Structurally it can be considered SiO_2 in which the NH^{2-} groups act like O^{2-} atoms.

The oxyhalides ($SiOHal_2$) and nitride halides (SiNHal) of silicon are also polymers.

In addition to its inorganic compounds, organosilicon compounds are of great importance. The simplest are the following:







Organosilicon compounds may be resins, rubbers, oils, etc., depending on the character of the chain and the nature of the terminal radicals. A common property of all organosilicon polymers is their relatively high thermostability (600 °C). A major contribution to their study has been made by K. A. Andrianov.

Organosilicon compounds are members of the broader class of *organoelement compounds*, the polymers of which combine the thermal stability of the inorganic materials with the elasticity and solubility of organic polymers. Methods have now been developed to synthesise polymers of organophosphorus, organoarsenic, organoantimony, organotitanium, organotin, organolead, organoboron, organo-

aluminium, and other compounds, most of which do not occur in nature. Thermostable polymers based on the following chains are being intensively studied:

Si—O—Si	Si—O—P	P—N—P
Si—O—Sn	Al—O—Al	B—N—B
Si—O—Ti	Ti—O—Ti	Si—N—P
Si—O—B	P—O—P	Al—P—Al
Si—O—Bi	Al—O—P	Sn—S—Sn
Si—O—Al	Si—N—Si	B—P—B

6.3. Germanium Subgroup

Germanium Ge, tin Sn, and lead Pb are full electron analogues. Their valence electrons are s^2p^2 electrons as in the typical elements of the group.

The involvement of the outer *s* electron pair diminishes in the formation of chemical bonds in the series Ge—Sn—Pb, only two (not four) electrons being involved. The most characteristic oxidation state of germanium (like carbon and silicon) is +4, and that of lead +2; the difference in tin's oxidation state in compounds is less marked though tin(IV) compounds are more stable.

The change in characteristic oxidation states in the C—Si—Ge—Sn—Pb series can be explained by secondary periodicity in the energy difference of *ns* and *np* orbitals (see Table 28). The stability of compounds in the series Ge < Sn ≪ Pb increases for compounds with a +2 oxidation state and decreases for compounds of E(IV), which is clearly seen from comparing the ΔG for the disproportionation of EO compounds:

$$Ge\ (c) + GeO_2\ (c) = 2GeO\ (c), \qquad \Delta G = 47\ kJ$$
$$Sn\ (c) + SnO_2\ (c) = 2SnO\ (c), \qquad \Delta G = -6\ kJ$$
$$Pb\ (c) + PbO_2\ (c) = 2PbO\ (c), \qquad \Delta G = -160\ kJ$$

The first reaction proceeds from right to left, i.e. GeO_2 is more stable than GeO. The third, on the contrary, proceeds from left to right: +4 is the more characteristic oxidation state of Ge, and +2 of Pb. This is also indicated by comparison of the standard electrode potentials of the corresponding processes:

$$GeO_2 + 4H^+ + 2e^- = Ge^{2+} + 2H_2O, \qquad E^\circ = -0.15\ V$$
$$PbO_2 + 4H^+ + 2e^- = Pb^{2+} + 2H_2O, \qquad E^\circ = 1.45\ V$$

Germanium is a dispersed element; the formation of ore concentrations is not characteristic of it. It is mainly associated with natural silicates and sulphides, and occurs in certain coals. The main tin mineral is *cassiterite* SnO_2 (*tinstone*) and the main lead mineral *galena*

PbS (*lead glance*). Lead is found in uranium and thorium minerals as the end product of radioactive decay of U and Th.

The simple substances. The metallic character of the simple substances increases markedly in the Ge—Sn—Pb series. Germanium is a greyish white substance (with a yellowish tint), resembling metal, but having a diamond-like lattice. Tin is polymorphous. Its common β modification (*white tin*) is a silvery white metal stable at temperatures above 13.2 °C; it has a tetragonal structure with octahedral coordination of the atoms. When cooled, it is converted into the α modification (*grey tin*) with a diamond-like structure (density, 5.85 g/cm³). The β → α transition is accompanied with an increase in specific volume (by 25.6 per cent) and the tin crumbles to a powder. Lead is a dark grey metal with the face-centred cubic structure typical of metals.

The change in structure of the simple substance over the Ge—Sn—Pb series corresponds to the change in their physical properties. Thus Ge (ΔE = 0.78 eV) and α Sn (ΔE = 0.08 eV) are semiconductors, while β Sn and Pb are metals. The transition from a predominantly covalent bond to a metallic one is accompanied with a loss of hardness in the simple substances; while germanium is quite hard and brittle, lead can be easily rolled into thin sheets.

Selected constants of the simple substances are given in the following table:

	C (diamond)	Si	Ge	β Sn	Pb
Density, g/cm³	3.52	2.33	5.32	7.29	11.34
M. p., °C	> 3500	1410	937	232	327
B. p., °C	—	3700	2830	2690	1750
Electrical conductivity*	—	—	0.001	8	5
ΔE, eV	5.6	1.12	0.78	(metals)	
d_{EE}, nm	0.154	0.234	0.244	0.316	0.350
$\Delta H^\circ_{subl.\ 298}$, kJ/mol	716	469	383	301	196
S°_{298}, J/K·mol	2.36	18.8	31.3	51.6	64.8
Hardness (diamond = 10)	10	7	6	1.8	1.5

The difference in structure of the simple substances affects their mutual solubility. Germanium and silicon are soluble in each other in any proportion in both the liquid and the solid states. Germanium, tin, and lead form solid solutions only within narrow limits; lead and tin only form eutectics with germanium and each other. The melting point of an alloy containing Sn 73.9 per cent and Pb 26.1 per cent is 181 °C.

It is not characteristic of germanium and its analogues to form metallic solid solutions but eutectic mixtures (Sn—Bi, Sn—Cd, Pb—Sn, Pb—Sb, Pb—Bi, etc.) are very typical.

* Electrical conductivity of mercury is taken as unity here and throughout the text.

Eutectic alloys of tin and lead are widely used. The most important alloys of tin and lead are the following: *type metal* (Pb 84-62 per cent, Sn 4-8 per cent, Sb 10-25 per cent, As 2-4 per cent), *bearing metal* (Pb or Sn 80-60 per cent with Sb and Cu additives) and low melting *solders* (Pb 80-60 per cent, Sn 17-40 per cent to Sb 2.5 per cent or Sn 90-50 per cent and the rest Pb).

The increase in the metallic attributes of the simple substances is also very marked in the character of the changes in chemical properties in the series Ge—Sn—Pb. In normal conditions Ge and Sn are stable in relation to air and water. Lead is oxidised in air and becomes coated with a bluish grey oxide film that deprives it of metallic lustre. At elevated temperatures Ge, Sn, and Pb react with most nonmetals to form compounds of Ge(IV), Sn(IV), and Pb(II), e.g. GeO_2, SnO_2, and PbO; $GeCl_4$, $SnCl_4$, and $PbCl_2$.

Germanium comes after hydrogen in the electromotive series and tin and lead immediately before it; germanium therefore does not react with dilute acids of the HCl and H_2SO_4 type. Insoluble salts $PbCl_2$ and $PbSO_4$ are formed on the surface of lead that protect it from further reaction with dilute hydrochloric and sulphuric acids. Tin and lead react with concentrated HCl to give $HECl_3$ and H_2ECl_4.

The differences in the chemical nature of the simple substances are especially marked in their relation to nitric acid. When oxidised with concentrated nitric acid, germanium is converted into germanic acid H_2GeO_3 ($GeO_2 \cdot nH_2O$) while tin is converted into stannic acid H_2SnO_3 ($EO_2 \cdot nH_2O$):

$$\underset{\text{Concentrated}}{E + 4HNO_3} = H_2EO_3 + 4NO_2 + H_2O$$

Tin behaves as a metal with dilute HNO_3, i.e. is converted to tin(II) nitrate:

$$\underset{\text{Dilute}}{3Sn + 8HNO_3} = 3Sn(NO_3)_2 + 2NO + 4H_2O$$

Lead behaves as a metal with HNO_3 of any concentration to form $Pb(NO_3)_2$.

When heated, tin and lead react with aqueous solutions of alkali:

$$\overset{0}{Sn} + 2KOH + 2H_2O = K_2[\overset{+2}{Sn}(OH)_4] + H_2$$

$$\overset{0}{Pb} + 2KOH + 2H_2O = K_2[\overset{+2}{Pb}(OH)_4] + H_2$$

Germanium dissolves in alkali only in the presence of an oxidant, e.g. H_2O_2:

$$\overset{0}{Ge} + 2KOH + 2H_2O_2 = K_2[\overset{+4}{Ge}(OH)_6]$$

Germanium is obtained from by-products of the refining of nonferrous metals and from the ash of certain coals and coking wastes.

Its compounds are converted first by a series of special operations to GeO_2, which is then reduced by hydrogen. The metal is further purified by zone refining. Most of the germanium produced is used in semiconductor apparatus.

Tin is produced by reducing cassiterite by carbon anthracite or coke. Large quantities of tin are recovered from tin-plated article (used tins), the tin being dissolved in alkaline solutions and then separated by electrolysis. Lead is obtained by converting lead glance to PbO, which is then also reduced by carbon.

Tin is mainly used to make *tin plate* which is largely used by the canning industry. *Tin foil* is used in the electrical engineering

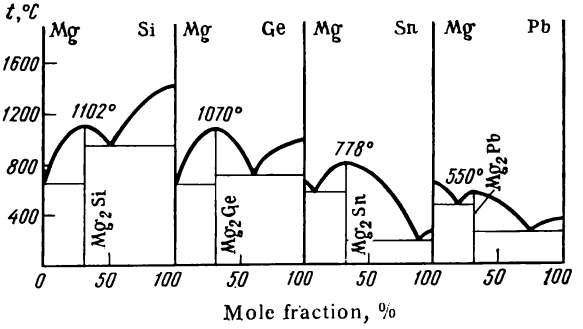


Fig. 175. **Phase** diagram of Mg—**Si, Mg—Ge,** Mg—Sn, and Mg—Pb systems

industry (in capacitors). Lead is used for accumulator plates, the casing of electric cables, corrosion-resistant materials for the chemical industry, and as a defence against radioactive radiation and X-rays. Both metals are used to make low-melting alloys.

Compounds of germanium, tin and lead (o. s. —4). The increasing metallic character of the simple substances in the Ge—Sn—Pb series is also seen in their behaviour with metals. Like silicon, germanium and its analogues form Mg_2E compounds (Fig. 175), which are called magnesium *germanide*, *stannide* and *plumbide* respectively. In the Mg_2Si—Mg_2Ge—Mg_2Sn—Mg_2Pb series the melting point, and width of the forbidden band diminish in accordance with the increasing proportion of the metal bonds.

	Mg_2Si	Mg_2Ge	Mg_2Sn	Mg_2Pb
M. p., °C	1102	1070	778	550
ΔE, eV	0.77-0.8	0.69-0.74	0.32-0.36	Metal

The tendency to form metallic compounds then increases in this series. Metallic compounds of tin and lead are usually formed with *s* elements, e.g., Na_2Sn, NaSn, $NaSn_2$.

Compounds of germanium(IV), tin(IV) and lead(IV). The stability of the binary compounds generally diminishes in the series Ge(IV)—Sn(IV)—Pb(IV) (see Fig. 131).

Oxides EO_2, fluorides EF_4, and chlorides ECl_4 are known for all three elements ($PbCl_4$ being quite unstable). Bromides EBr_4 and iodides EI_4, sulphides ES_2, and nitrides E_3N_4 are known only for Ge(IV) and Sn(IV).

The coordination number of germanium and its analogues with a +4 oxidation state is usually six or four, which corresponds to octahedral and tetrahedral unit cells. As the atoms become bigger in the transition from C and Si to the Ge—Sn—Pb series, the four coordination number becomes less characteristic, while six, on the contrary, becomes more typical.

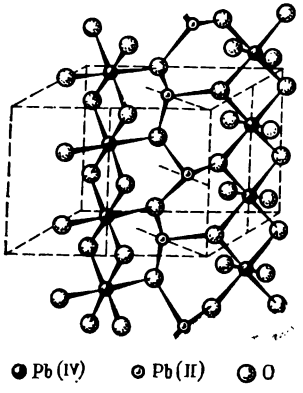


Fig. 176. Structure of red lead Pb_3O_4

Unlike SiO_2, crystals of GeO_2, SnO_2 and PbO_2 have a rutile-type structure (see Fig. 70*b*), but a high-temperature form of GeO_2 with a quartz-type structure is also known.

The *dioxides* GeO_2 and SnO_2 (both white), like SiO_2, are refractory (1100 °C to 2000 °C). Dark brown PbO_2 decomposes when heated. Germanium dioxide, like SiO_2, is easily vitrified. The addition of GeO_2 to quartz glass gives it high transparency and strong refractive properties, which makes GeO_2 very important in the manufacture of optical glass. Tin dioxide is used to make enamels and glazes in the ceramics industry.

The dioxides are chemically inactive and do not dissolve in water. Basic properties increase slightly in the GeO_2—SnO_2—PbO_2 series. Like SiO_2, GeO_2 is an acidic compound and is soluble in hot alkalis. SnO_2 is amphoteric, it reacts with concentrated H_2SO_4 when heated to give $Sn(SO_4)_2$. The dioxides of lead and tin react with alkalis by fusion. When EO_2 is fused with alkalis or the corresponding oxides, the following compounds are formed: $\overset{+1}{M}_2EO_3$ and $\overset{+2}{M}EO_3$, $\overset{+1}{M}_4EO_4$, and $\overset{+2}{M}_2EO_4$:

$$2CaO + PbO_2 = Ca_2PbO_4$$

$$2PbO + PbO_2 = Pb_2PbO_4\ (Pb_3O_4)$$

In contrast to oxysilicates, the unit cell of oxystannates and oxyplumbates is an EO_6 octahedron. The crystals of orthostannate Ba_2SnO_4 and orthoplumbate Ca_2PbO_4 are formed by EO_6 octahedra united by their four apexes into layer lattices (as in Fig. 177). The crystals of metastannates $\overset{+2}{M}SnO_3$ (M = Ca, Sr,

Ba, Cd) have a perovskite-type lattice (see Fig. 73). The crystals of Pb_2PbO_4 have chains of PbO_6 octahedra with common edges (see Fig. 176). The chains are connected together by three coordination Pb(II) atoms. The unit cell of oxygermanates may be GeO_4 tetrahedra or GeO_6 octahedra which explains their greater variability compared with oxysilicates.

Only the oxygermanates, oxystannates, and oxyplumbates of alkali metals are soluble in water; their solutions are strongly hydrolysed.

Red lead oxide Pb_2PbO_4 (Fig. 176) can be regarded as an orthoplumbate(IV) of lead(II). The different valencies of the lead atoms in Pb_3O_4 can be readily demonstrated by reacting it with dilute nitric acid: an exchange reaction takes place that yields derivatives of Pb(II) and Pb(IV):

$$Pb_2PbO_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Red lead (orange-red in colour) is used in the manufacture of paints to protect metals against corrosion and high-temperature cements, as an oxidant, and so on.

It is very difficult to isolate germanic, stannic, or plumbic acids (like silicic acids) in the free state: attempts to isolate them end in the formation of colloid solutions that are converted into gel-like precipitates of a varied and indefinite $EO_2 \cdot nH_2O$ composition.

The action of aqueous solutions of ammonia on $SnCl_4$ solutions initially gives hexahydroxystannic acid

$$SnCl_4 + 4H_3N + 6H_2O = H_2[Sn(OH)_6] + 4NH_4Cl$$

On standing the acid is more or less quickly polymerised and precipitates $SnO_2 \cdot nH_2O$. Freshly precipitated stannic and plumbic acids are soluble in acids and alkalis. In the latter case they form hydroxy compounds of the $\overset{+1}{M}_2[E(OH)_6]$ type

$$EO_2 + 2KOH + 2H_2O = K_2[E(OH)_6]$$

The change in structure and composition of stannic acids is accompanied with a change in their chemical activity. The fresh precipitate of the acid (*α-stannic acid*) is easily soluble in alkalis and even in acids, but after standing (now being *β-stannic acid*) it reacts (like SnO_2) only with molten alkalis. The inactive form of stannic acids (β-stannic acid) is also formed by the oxidation of tin in concentrated nitric acid. The different chemical activity of α- and β-stannic acids is due to their different structures: a decrease in the number of active OH groups, and the formation of stable Sn—O—Sn bonds, in the transition from the alpha to the beta forms.

The *disulphides* GeS_2 (white) and SnS_2 (yellow) are insoluble in water and dilute acids. They are formed by the action of H_2S on acidified solutions of E(IV) derivatives, e.g.

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

Being acidic, ES_2 react with alkalis and basic sulphides:

$$ES_2 + (NH_4)_2S = (NH_4)_2ES_3$$

Acids corresponding to sulphide germanates(IV) and sulphide stannates(IV) decompose as soon as obtained:

$$(NH_4)_2ES_3 + 2HCl = H_2ES_3 + 2NH_4Cl$$
$$H_2ES_3 = ES_2 + H_2S$$

Yellow scales of lead disulphide SnS_2 (artificial gold leaf) are used as mosaic gold, to 'gild' wood, etc.

The molecules of the *tetrahalides* $EHal_4$ have a tetrahedral shape with the E atom in the centre. As the size of the orbitals increases in the $GeHal_4$—$SnHal_4$—$PbHal_4$ series the molecules become much less stable. Lead tetrabromide and tetraiodide are not known.

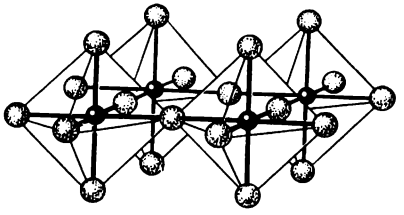


Fig. 177. Structure of SnF_4

The tetrahalides, except SnF_4 and PbF_4, have molecular lattice in the solid state (Fig. 177), so that they are low-melting and volatile. In ordinary conditions GeF_4 is a gas, $EHal_4$ are liquids.

Except for an orange GeI_4 and yellow SnI_4 and $PbCl_4$, the tetrahalides of germanium and its analogues are colourless.

The steep increase in boiling and melting (freezing) points in the transition from GeF_4 (f.p., —15 °C) to SnF_4 (m.p., 200 °C) and PbF_4 (m.p., 600 °C) corresponds to the transition from a molecular lattice to a polymeric one. Crystals of SnF_4 and PbF_4 have layer lattices consisting of EF_6 octahedral unit cells (Fig. 177). The lead atom in PbF_4 thus has a stable coordination number of six so that, unlike all the other halides of lead(IV), it is stable.

Because of their coordination unsaturation, the molecules of tetrahalides with a molecular structure are chemically active. Like other covalent compounds of this type (see hydrolysis of $SiCl_4$), their hydrolysis proceeds through a stage of attachment of the water molecule and a stage of elimination of the hydrogen halide molecules, to the formation of hydroxides

$$SnCl_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HCl$$

which are polymerised into hydrated oxides, e.g. $SnO_2 \cdot nH_2O$.

The tetrahalides also react with basic halides

$$2KF + EF_4 = K_2[EF_6]$$

Fluorocomplexes GeF_6^{2-} are characteristic of Ge(IV), like Si(IV), but an unstable $Cs_2[GeCl_6]$ is also obtained with Ge(IV). Complex halides of all types from $\overset{+1}{M_2}[\overset{+4}{E}F_6]$ to $\overset{+1}{M_2}[\overset{+4}{E}I_6]$ are known for Sn(IV) and Pb(IV), which points to stabilisation of the +4 oxidation state in lead in anion complexes with a coordination number of six. The halogen complexes of germanium and tin are stable both in solution and in crystalline compounds. The similar compounds of lead are easily hydrolysed.

The most important tetrahalide is $SnCl_4$. In normal conditions it is a liquid, that fumes in air because of hydrolysis. $SnCl_4$ is prepared by the action of dry chlorine on liquid tin, a reaction that is used in one of the methods of recovering tin from tin-plated scrap. $SnCl_4$ and $(NH_4)_2SnCl_6$ are mainly used as a mordant in dyeing and for preparing other compounds of tin.

Tin tetrachloride is readily soluble in low-polar solvents and is a good solvent of iodine, sulphur, phosphorus, etc.

The *hydrides* of elements of the germanium subgroup are few in number and unstable, owing to the further loss of stability of the E—E and E—H bonds in the Ge—Sn—Pb series compared with the Si—Si and Si—H bonds.

Selected constants of the hydrides EH_4 are given in the following table:

	CH_4	SiH_4	GeH_4	SnH_4	PbH_4
$\Delta H^\circ_{f,\,298}$, kJ/mol	—75	35	91	163	250
E_{EH}, kJ/mol	414	320	291	258	205
d_{EH}, nm	0.109	0.148	0.153	0.170	—
M. p., °C	—184	—185	—166	—150	—
B. p., °C	—161	—112	—88	—52	—
Decom. point, °C	800	450	285	150	0

The table shows that stability diminishes in the series SiH_4 (*silane*)—GeH_4 (*germane*)—SnH_4 (*stannane*)—PbH_4 (*plumbane*). Plumbane is so unstable that its existence can only be demonstrated indirectly. As germane and stannane are passed through a hot-red glass tube, they decompose and are deposited in the form of a metal mirror.

Hydrides of E(IV) are isolated by the action of dilute acids on certain germanides and stannides:

$$Mg_2E + 4HCl \xrightarrow[\text{in water}]{} 2MgCl_2 + EH_4$$

$$Mg_2E + 4NH_4Cl \xrightarrow[\substack{\text{in liquid}\\ H_3N}]{} 2MgCl_2 + EH_4 + 4H_3N$$

In the reaction of Mg_2Ge with acids, *digermane* Ge_2H_6 (m.p. —109 °C, b. p. 31 °C) and *trigermane* Ge_3H_8 (m.p. —106 °C, b.p. —52 °C) are also formed in addition to GeH_4. More complicated germanes and a *distannane* Sn_2H_6 are also known.

Compounds of germanium(II), tin(II) and lead(II). The coordination numbers of elements of the germanium subgroup with a +2 oxidation state are more varied than in the +4 oxidation state (3, 4, 5, and 6). Atoms of E(II) have a nonbonding electron pair, so that the coordination numbers 3, 4, 5, and 6 correspond to a tri-

gonal pyramid (type AB_3E; see Fig. 51*b*), distorted tetrahedron (type AB_4E; see Fig. 51*e*), tetragonal pyramid (type AB_5E, see Fig. 51*i*) and a distorted octahedron (type AB_6E).

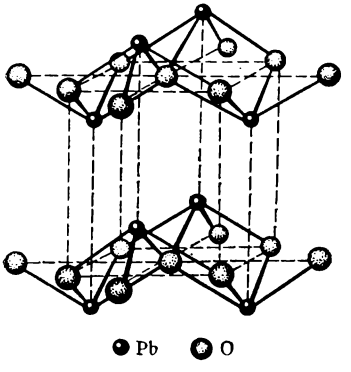


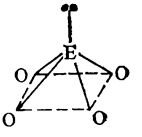
Fig. 178. Structure of PbO

The +2 oxidation state is more characteristic of lead and is displayed in its various compounds, while only a few binary compounds are known for germanium(II).

Most derivatives of Pb(II) are crystalline solids. Except for the nitrate $Pb(NO_3)_2$ and acetate $Pb(CH_3COO)_2$, they are poorly soluble ($PbHal_2$) or almost insoluble ($PbSO_4$, $PbCrO_4$, $PbCO_3$) in water, which explains resistance of lead to the action of most acids.

Compounds of E(II) are usually colourless but some are coloured: the oxides GeO and SnO being black, PbO red or yellow, the sulphides GeS and SnS brown, PbS black, the iodide SnI_2 red, PbI_2 yellow, and so on.

The crystal structure of E(II) compounds is very complicated; SnO and red PbO, for example, have a layer lattice (Fig. 178) formed by EO_4 tetragonal pyramids with a localised electron pair at the E atom:



The oxides EO and hydroxides $E(OH)_2$ are amphoteric, and react with both acids and alkalis:

$$E(OH)_2 + 2HCl = ECl_2 + 2H_2O$$
$$E(OH)_2 + KOH = K[E(OH)_3]$$

Basic properties predominate in derivatives of Pb(II) and acidic ones in those of Ge(II).

The stability of hydroxystannates(II) and hydroxyplumbates(II) known as *hydroxystannites* and *hydroxyplumbites*, is lower than that of similar derivatives of E(IV). They exist only in solutions in the presence of excess alkali and decompose otherwise. Crystalline salts $Na[Sn(OH)_3]$, $Ba[Sn(OH)_3]_2$, and $Na_2[Pb(OH)_4]$ have been isolated.

The tendency to form complexes is weaker in the dihalides $EHal_2$ than in $EHal_4$. Dihalides react with basic halides to give complexes of the $M^{+2}[EHal_3]$ and $M^{+2}_2[EHal_4]$ type. The formation of complex

halides is explained by the higher solubility of lead(II) halides in the presence of hydrohalic acids than in water. The complex halides decompose in dilute solutions.

Derivatives of Ge(II) and Sn(II) are strong reducing agents. $GeCl_2$ reacts almost instantaneously with Cl_2, and $SnCl_2$ reacts rapidly at room temperature, but $PbCl_2$ does not react at all with chlorine in normal conditions. Derivatives of Ge(II) and Sn(II) reduce certain metals from their compounds, e.g.

$$2Bi(NO_3)_3 + 3Na[Sn(OH)_3] + 9NaOH = 2Bi\downarrow + 3Na_2[Sn(OH)_6] + 6NaNO_3$$

They also convert Fe^{3+} into Fe^{2+}, CrO_4^{2-} into Cr^{3+}, etc.

Unlike PbS, GeS and SnS are oxidised by ammonium polysulphides to ES_2, which then react with $(NH_4)_2S$ to form compounds $(NH_4)_2ES_3$ soluble in water:

$$SnS + (NH_4)_2S_2 = SnS_2 + (NH_4)_2S$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$

This reaction is used to separate SnS and PbS from each other.

The reducing properties of Sn(II) derivatives are employed in chemical synthesis and analysis.

Compounds of Pb(IV), on the contrary, are strong oxidants, particularly in an acidic medium even, for example, oxidising Mn^{2+} to MnO_4^-.

$$2Mn^{2+} + 5PbO_2 + 4H^+ = 5Pb^{2+} + 2MnO_4^- + 2H_2O$$

PbO_2 and Pb_3O_4 are used as oxidants in the manufacture of matches.

The conversion of Pb(II) to Pb(IV) is only possible through electrochemical oxidation or by the action of the strongest oxidants (Cl_2, chloride of lime, etc.) when heated in an alkaline medium, for example

$$Pb(CH_3COO)_2 + Cl_2 + 4KOH = PbO_2 + 2KCl + 2KCH_3COO + 2H_2O$$

Pb(II) compounds are used as follows: PbO in the manufacture of optical glass, flint glass (crystal), glazes, and drying oils; $PbCrO_4$ (orange-red) in mineral paints; $2PbCO_3 \cdot Pb(OH)_2$ as a constituent of lead white. Barely soluble SnF_2 is used as an additive to tooth pastes. Organotin and organolead compounds have acquired great practical and theoretical importance in recent years.

6.4. Oxycompounds of the *p* Elements of Group IV, V, VI and VII

A survey of the chemistry of Group IV, V, VI, and VII *p* elements shows that the number and stability of oxy compounds increase steeply in the series E(VII)—E(VI)—E(V)—E(IV). To explain this, let us consider the oxy compounds of the Cl(VII)—S(VI)—P(V)—Si(IV)

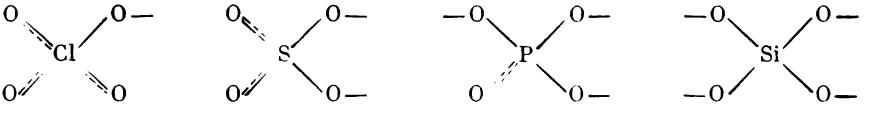
series. The coordination number of these elements in their highest oxidation state is four, which corresponds to a tetrahedral unit cell

$$\cdot\dot{C}lO_4 \quad \cdot\dot{S}O_4 \quad \cdot\dot{P}O_4\cdot \quad \cdot\dot{\dot{S}}iO_4\cdot$$

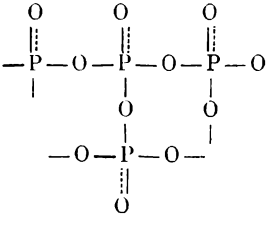
(The dots indicate the number of unpaired electrons.) These radicals are unstable in the free state and are converted into tetrahedral ions through the acceptance of electrons:

$$ClO_4^- \quad SO_4^{2-} \quad PO_4^{3-} \quad SiO_4^{4-}$$

or they form compounds with one, two, three, and four bonds respectively:



Thus, in the case of chlorine(VII), there is only one possible way of joining the oxychlorate tetrahedra (see Table 10), namely, by their uniting into a dimer with formation of Cl_2O_7 molecules. Sulphur(VI) forms both a dimer $S_2O_7^{2-}$ and open $(SO_3)_\infty$ and closed $(SO_3)_3$ chains. Each oxysulphate tetrahedron unites with a neighbour through its two apexes (two oxygen bridge atoms). With phosphorus(V) compounds we observe another method of the joining of oxyphosphate tetrahedra: three oxygen bridge atoms are involved in the formation of branched chains

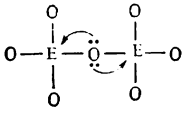


and a layered form of $(P_2O_5)_{2\infty}$. Finally, for silicon(IV), apart from these types of bridge structure, a trimeric polymer $(SiO_2)_{3\infty}$ can be formed, the role of the bridge atoms in the polymer being played by four of the oxygen atoms of each oxysilicate tetrahedron.

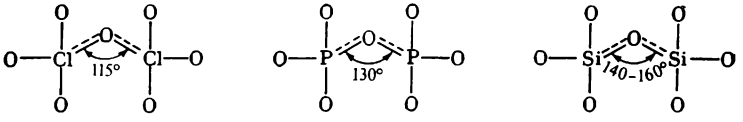
The increasing number of ways in which tetrahedral unit cells are joined accounts for the steep increase in the number of oxycompounds formed by elements of the Cl(VII)—S(VI)—P(V)—Si(IV) series (see Table 10).

The increasing stability of the E—O—E type heterochain in the Cl—S—P—Si series is governed by the superimposition of a π bond arising from the involvement of the E atom's free *d* orbitals and the unshared $2p$ electron pairs of the

oxygen bridge atom



The bond angle ∠ EOE is straightened with the formation of an additional bond in the E—O—E chain. The angle ∠ EOE will evidently increase with the strength of π bond:

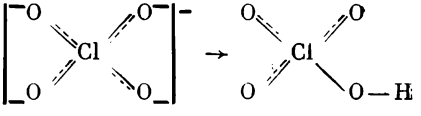


Hybridisation theory explains the decreasing stability in the SiO_4^{4-}—PO_4^{3-}—SO_4^{2-}—ClO_4^- series by a lowering of the stability of the central atom's sp^3 hybrid state owing to the increasing energy difference between the 3*s* and 3*p* levels (see Table 28). The importance of π bonds in stabilising the sp^3 hybrid state of the central atom increases in this series. This idea is used to explain the shortening of the d_{EO} bond length in the SiO_4^{4-}—PO_4^{3-}—SO_4^{2-}—ClO_4^- series compared with single bonds (see Table 42).

Table 42. **Bond Length in Tetrahedral Ions**

Bond	Bond length, nm		Shortening of bond length, nm	Bond	Bond length, nm		Shortening of bond length, nm
	E — O	E ... O			E — O	E ... O	
SiO	0.176	0.163	0.013	SO	0.169	0.149	0.020
PO	0.171	0.154	0.017	ClO	0.168	0.145	0.023

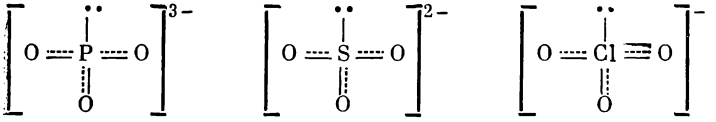
Thus, while the stability of the SiO_4^{4-} ion is mainly to sigma bonds the stability of the ClO_4^- ion also depends substantially on π bonds. The number of σ bonds in the chlorine-oxygen tetrahedron of the ionic $KClO_4$ and covalent $HClO_4$ is the same but, because of the presence of an O—H bond in $HClO_4$, the involvement of the electrons in π bonds is less significant



which substantially alter the stability of the compounds: $KClO_4$ begins to decompose only at 400 °C, while $HClO_4$ explodes when slightly heated. On the contrary, since the framework of sp^3 bonds is quite stable in the SiO_4^{4-} ion, the breakdown of π bonds does not significantly affect its stability. All the four oxygen atoms in the SiO_4^{4-} ion can therefore form second σ bonds.

In accordance with the decreasing sensitivity of the EO_4^{n-} ion to breakdown of π bonds and formation of O—H σ bonds, stability increases in the series $HClO_4$—H_2SO_4—H_3PO_4—H_4SiO_4 while oxidising activity decreases. In other words, the contrapolarising effect of the protons diminishes.

The decreasing tendency to sp^3 hybridisation in the transition from Si to Cl also explains the increasing stability of anions in the PO_3^{3-}—SO_3^{2-}—ClO_3^- series



Being a marked donor of the unshared electron pair of the phosphorus atom, the PO_3^{3-} ion attaches a proton and is converted into a tetrahedral ion PO_3H^{2-}, or is oxidised to PO_4^{3-} ion. There is an SO_3^{2-} ion, but it is easily oxidised to SO_4^{2-} to give SO_3H^-. As for the ClO_3^- ion, an sp^3 hybrid state is not characteristic of Cl, so that the unshared electron pair (s^2) remains a sphere and does not display any tendency to a donor-acceptor interaction. The ClO_3^- ion is therefore quite stable and scarcely displays reducing properties. Thus reducing activity decreases in the PO_3^{3-}—SO_3^{2-}—ClO_3^- series.

The stability of the tetrahedral oxy anions of fourth period *p* elements decreases along with the diminishing stability of the sp^3 hybrid state of the central atom in the series GeO_4^{4-}—AsO_4^{3-}—SeO_4^{2-}—BrO_4^-. Oxidising activity increases markedly in the same series. These ions are less stable while the AsO_4^{3-}, SeO_4^{2-} and BrO_4^- ions are stronger oxidants than the corresponding anions of third period *p* elements.

Since a coordination number of six, rather than four, is more characteristic of fifth period *p* elements, uniform changes in properties are not observed in the vertical series

ClO_4^-	SO_4^{2-}	PO_4^{3-}	SiO_4^{4-}
BrO_4^-	SeO_4^{2-}	AsO_4^{3-}	GeO_4^{4-}
IO_6^{5-}	TeO_6^{6-}	SbO_6^{7-}	SnO_6^{8-}

The structure of oxy compounds of I(VII), Te(VI), Sb(V) and Sn(IV), and hence their properties, differ substantially from those of similar compounds of Cl(VII) and Br(VII), S(VI) and Se(VI), P(V) and As(V), Si(IV) and Ge(IV).

CHAPTER 7

Group III *p* Elements

The group III *p* elements comprise the typical elements boron and aluminium and the elements of the gallium subgroup viz., gallium, indium, and thallium

B	$1s^2 2s^2 2p^1$
Al	$2s^2 2p^6 3s^2 3p^1$
Ga	$3s^2 3p^6 3d^{10} 4s^2 4p^1$
In	$4s^2 4p^6 4d^{10} 5s^2 5p^1$
Tl	$4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$

Selected constants of these elements are as follows:

	$_5$B	$_{13}$Al	$_{31}$Ga	$_{49}$In	$_{81}$Tl
Atomic mass	10.81	26.98	69.72	114.82	204.37
Valence electrons	$2s^2 2p^1$	$3s^2 3p^1$	$4s^2 4p^1$	$5s^2 5p^1$	$6s^2 6p^1$
Metallic atom radius, nm	0.091	0.143	0.139	0.166	0.171
Covalent atom radius, nm	0.088	0.126	0.127	0.144	0.147
Conventional radius of E^{3+}, ion, nm	0.020	0.057	0.062	0.092	0.105
Ionisation energy $E^0 \rightarrow E^+$, eV	8.298	5.986	5.998	5.78	6.11
Abundance, mole per cent	6×10^{-4}	6.6	4×10^{-4}	1.5×10^{-6}	3×10^{-5}

As will be seen from the table the ionisation energy of the atoms of these elements decreases with increasing atomic number: boron is a nonmetal, thallium is a typical element—metal.

7.1. Boron

Compared with the second period elements considered above there is a weakening of the nonmetallic character of the element in boron. In this respect it resembles silicon (diagonal likeness in the periodic system). Compounds in which the oxidation state of boron is +3 are most characteristic of it. Negative oxidation states are rare; with metals boron usually forms nonstoichiometric compounds.

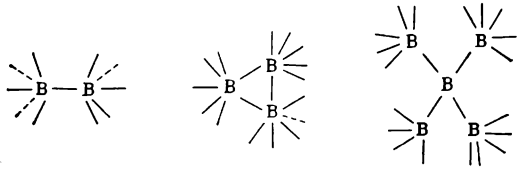
The abundance of boron in the Earth's crust is 6×10^{-4} mole per cent. It occurs as two isotopes, viz., ^{10}B (19.57 per cent) and ^{11}B (80.43 per cent). Its main minerals are borates: *borax* $Na_2B_4O_7 \times 10H_2O$, *kernite* $Na_2B_4O_7 \cdot 4H_2O$, *sassolite* H_3BO_3.

Its relatively low abundance, which does not correspond to its low atomic number, is explained by the high reactivity of its nuclei with neutrons:

$$^{10}_5B + ^1_0n = ^4_2He + ^7_3Li$$

Boron's capacity to absorb neutrons is the reason for the importance of boron-containing materials in nuclear power engineering, in which they are used as moderators and as biological protection.

The simple substances. Boron has several allotropic forms in which its atoms are united in B_{12} groupings, with an *icosahedral* configuration (Fig. 179). The arrangement of the icosahedra with respect to one another is as follows:



The crystals of boron are black. It is a high-melting (m.p., 2300 °C, b.p., about 2550 °C), diamagnetic substance with semiconductor properties (ΔE = 1.55 eV).

In normal conditions it is, like silicon, quite inactive and reacts directly only with fluorine. When heated (400 °C to 700 °C), it is oxidised by oxygen, sulphur, chlorine, and even nitrogen (at temperatures above 1200 °C). Boron does not react with hydrogen. When strongly heated it becomes a reducing agent for stable oxides like SiO_2, P_2O_5, etc.

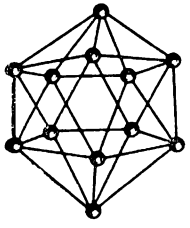


Fig. 179. Icosahedral grouping of B_{12} atoms

$$3SiO_2 + 4B = 3Si + 2B_2O_3$$

This is explained by the high Gibbs' energy of formation of boron oxide B_2O_3 ($\Delta G^\circ_{f,298}$ = = −1178 kJ/mol).

Only hot concentrated nitric and sulphuric acids, and aqua regia, react with boron, converting it into H_3BO_3. In the absence of oxidants, alkalis do not react with boron.

Because of the high Gibbs' energies of most boron compounds, the pure element is usually obtained by *metallothermy* (generally by reduction by magnesium or sodium):

$$B_2O_3 + 3Mg = 3MgO + 2B, \quad \Delta G^\circ_{298} = -515 \text{ kJ}$$

$$KBF_4 + 3Na = 3NaF + KF + B, \quad \Delta G^\circ_{298} = -389 \text{ kJ}$$

Amorphous boron, which can be converted to the crystalline state by recrystallisation in molten metals, is obtained in this way. This method, however, yields a product contaminated with impurities. Pure boron (99.5 per cent) is obtained by electrolysis of molten fluoborates. The purest boron is prepared by thermal decomposition of vapours of boron bromide on hot tantalum wire (1000 °C to 1200 °C)

in the presence of hydrogen:

$$2BBr_3 + 3H_2 = 2B + 6HBr$$

or by decomposition (cracking) of its hydrogen compounds

$$B_2H_6 = 2B + 3H_2$$

Metallic compounds of boron. Boron forms borides with metals of an average composition M_4B, M_2B, MB, M_3B_4, MB_2, MB_6.

One and the same element can form borides of different composition depending on the conditions, e.g. Nb_2B, Nb_3B_2, NbB, Nb_3B_4, NbB_2; Cr_4B, Cr_2B, CrB, Cr_3B_4, CrB_2. The structure of the borides becomes much more complicated as the boron content increases. In borides of the M_4B and M_2B type the boron atoms are isolated from each other; in the M_3B_2 type they are united in pairs, in MB compounds in chains, in M_3B_4 in twin chains, in MB_2 in a network of six-member rings; finally, in MB_6 and MB_{12} borides, the atoms are in trimeric frames of octahedral and icosahedral groups respectively.

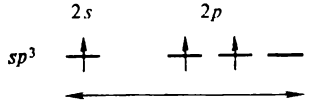
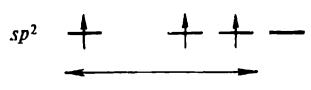
Most borides of *d* and *f* elements are very hard, refractory (2000 °C to 3000 °C), and chemically stable. Those of *s* elements are chemically active and are decomposed, for example, by acids with the formation of a mixture of boron hydrides.

Refractory, heat-resistant borides of *d* elements (Cr, Zr, Ti, Nb, Ta) and their alloys are used in jet engines, the vanes of gas turbines, etc. Certain borides can also be used as catalysts, as cathode material for electrical instruments, and so on.

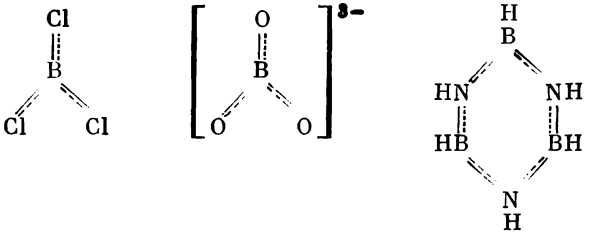
Compounds of boron(III). Boron has an oxidation state of +3 in compounds with elements more electronegative than itself, i.e. in halides, oxide, sulphide, nitride, hydrides, and corresponding borate complexes, the simplest of which are the following:

BF_3	B_2O_3	BH_3
BF_4^-	BO_2^-	BH_4^-

The coordination number of boron(III) is four or three, depending on the number of σ bonds which corresponds to sp^3 or sp^2 hybridisation of its valence orbitals.

Hybridisation of boron orbitals	Arrangement in space of σ bonds	Typical compounds
	tetrahedral	BF_4^-, BH_4^-
	triangular	BCl_3, BO_3^{3-}

The sp^2 hybridisation of the valence orbitals of boron accounts for the planar, triangular structure of the molecules, complexes, and unit cells of its compounds. As with carbon, the sp^2 hybrid state is stabilised by a nonlocalised $\pi p-\pi p$ bond formed by a free $2p$ orbital of the boron atom and an unshared electron pair of the atoms connected with it:



A partial double bond arises as a result; bond strength increases and the internuclear distance diminishes.

The d_{BO} bond length with a triangular arrangement (0.136 nm), for instance, is 0.012 nm shorter than with the tetrahedral arrangement (0.148 nm). Similarly, the d_{BF} bond length in BF_3 (0.129 nm) is shorter than in BF_4^- (0.143 nm), while the force constant k_{BF} of the bond in BF_3 is higher (718 N/m) than in BF_4^- (528 N/m).

In accordance with its stable coordination number, its binary halides $BHal_3$ are monomolecular while the oxide B_2O_3, sulphide B_2S_3, and nitride BN are polymers. Boron hydrides have a very characteristic structure.

The binary compounds of boron(III) are acidic, as is shown, for example, by the character of their solvolysis (hydrolysis) and their interaction with basic compounds.

Boron *halides* of the $BHal_3$ type are known for all the halogens. They can be obtained from the simple substances by heating. All are colourless. The molecules of $BHal_3$ are planar triangles with the boron atoms at the centre (an sp^2 hybrid state of boron). In normal conditions BF_3 is a gas, BCl_3 and BBr_3 liquids, and BI_3 a solid.

	BF_3	BCl_3	BBr_3	BI_3
M. p., °C	−127	−107	−46	+43
B. p., °C	−101	−12.5	+90	decomp.
$\Delta H^\circ_{f,\,298}$, kJ/mol	−1137	−427	−243	−38
$\Delta G^\circ_{f,\,298}$, kJ/mol	−1120	−387	−238	—
d_{BHal}, nm	0.129	0.173	0.187	0.210
E_{BHal}, kJ/mol	644	443	376	284
k_{BHal}, N/m	720	320	250	200

In the solid state, boron halides have molecular lattices. As the bond length increases and energy diminishes in the BF_3—BCl_3—BBr_3—BI_3 series, the stability of the compounds markedly decreases.

This is also evident from the character of changes in their enthalpies and Gibbs' energies of formation.

The halides most commonly employed are BF_3 and BCl_3. The trifluoride is obtained by heating B_2O_3 with CaF_2 in the presence of concentrated sulphuric acid (cf. the preparation of SiF_4, p 416):

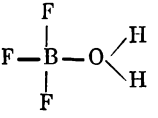
$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 2BF_3 + 3CaSO_4 + 3H_2O$$

Boron trichloride (as $SiCl_4$) is obtained by chlorinating a hot mixture of the oxide and carbon

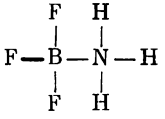
$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$$

Boron trihalides are strong acceptors of electron pairs, BF_3 uniting, for example, with the molecules of water, ammonia, alcohol, ether, etc.

The reaction of BF_3 with water gives $BF_3 \cdot H_2O$ (m.p. 10.2 °C, decomposes at 20 °C):



With ammonia a solid substance $BF_3 \cdot NH_3$ (m.p. −163 °C) is formed



that is readily soluble in water without appreciable hydrolysis. In the products of combination the boron atoms are in an sp^3 hybridisation state.

The use of boron trifluoride and boron trichloride as catalysts in organic synthesis is determined by their capacity for a donor-acceptor interaction.

The acidic nature of boron trihalides is displayed, for example, in their hydrolysis, which is irreversible and yields acids

$$BHal_3 + 3HOH = H_3BO_3 + 3HHal$$

Because of this BCl_3 and BBr_3 fume in damp air, while BI_3 explodes with water. The acidic character of BCl_3 is seen in its reaction with liquid ammonia:

$$BCl_3 + 6H_3N = B(NH_2)_3 + 3NH_4Cl$$

The boron(III) *oxide* B_2O_3 exists in several forms. The boron atoms in its crystals are located inside a BO_3 equilateral triangle or BO_4 tetrahedron of oxygen atoms. Crystalline B_2O_3 (m.p. 450 °C, b.p. 2250 °C) has high formation enthalpies ($\Delta H_f^\circ = -1254$ kJ/mol) and Gibbs' energy of formation ($\Delta G_f^\circ = -1194$ kJ/mol). It is easily

vitrified but is very difficult to crystallise. The oxide B_2O_3 is prepared by dehydrating H_3BO_3.

In contrast to the Si—O—Si chain, the B—O—B chain is comparatively easily broken during hydration; in this respect oxygen compounds of boron(III) are similar to those of phosphorus. Being an acidic anhydride, B_2O_3 reacts vigorously with water to form boric acid H_3BO_3.

Boron *sulphide* B_2S_3 is a glassy substance, which is completely decomposed in water.

In accordance with the stable coordination numbers of boron (three and four), the *nitride* BN exists in two forms. That formed by interaction of the simple substances has a hexagonal, atom-layer structure of graphite type (see Fig. 166*b*). The hexagonal rings of boron nitride contain alternating atoms of boron and nitrogen (spaced at a distance of 0.145 nm and an angle of 120°), which corresponds to sp^2 hybridisation of the valence orbitals of both. (The layers of boron nitride are 0.334 nm apart, i.e. closer to one another than in graphite—0.340 nm). In contrast to graphite, boron nitride is white (white graphite). It is a semiconductor (ΔE = 4.6-3.6 eV); it scales easily, and resistant to high temperatures (m.p. about 3000 °C). It decomposes very slowly in water when heated, decomposition is accelerated in the presence of dilute acids.

The other form of boron nitride (*borazon*) consists of boron and nitrogen atoms in the sp^3 hybridisation state, and has a crystal lattice of the diamond type (see Fig. 166*a*). It is formed from hexagonal boron nitride under high pressures of the order of 6 to 8 HPa and a temperature of 1800 °C. The conversion is similar to that of graphite into diamond.

Borazon crystals may be either coloured (from yellow to black) or colourless. Borazon is very hard, and in this respect is almost comparable with diamond (some samples of borazon can even leave traces on diamond). Its mechanical strength and thermal stability are higher than those of diamond; when it is heated in vacuum to 2700 °C, for example, it remains unaltered; when heated to 2000 °C in air, its surface is only slightly oxidised, whereas diamond burns at 900 °C. Like diamond, borazon is a dielectric. Its valuable properties account for its importance in engineering.

Boron *hydrides* (*boranes*) are similar in properties to silanes and are obtained in the same way. As a rule, a mixture of boranes and hydrogen is obtained by the action of acids on certain chemically active borides, e.g.

$$6MgB_2 + 12HCl = H_2 + B_4H_{10} + 6MgCl_2 + 8B\}$$

The simplest hydrogen compound of boron BH_3 does not exist in normal conditions, because it is coordinationally unsaturated and unable to form delocalised π bonds that could stabilise sp^2 hybrid

state of the boron atom. Coordinational saturation of boron atoms is possible when these radical-molecules combine with each other, e.g.

$$BH_3\,(g) + BH_3\,(g) = B_2H_6\,(g), \quad \Delta G^\circ_{298} = -127\ kJ$$

The simplest B_nH_{n+4} and B_nH_{n+6} boron hydrides that have been isolated in the free state are the gases B_2H_6 and B_4H_{10}, the liquids B_5H_9 and B_6H_{10}, and the solid $B_{10}H_{14}$.

	B_2H_6	B_4H_{10}	B_5H_9	B_6H_{10}	$B_{10}H_{14}$
M. p., °C	—166	—120	—47	—65	99
B. p., °C	—92.5	18	48.6	?	213(?)

The Gibbs' constant for all boranes is $\Delta G^\circ_f \gg 0$, so that they are obtained indirectly.

It will be quite clear from the table above that boron hydrides are electron-deficient. The total number of valency electrons in B_2H_6, for example, is 12, which is insufficient to form eight single two-electron two-centre bonds. Diborane B_2H_6 has two- and three-centre bonds (Fig. 180). The two terminal BH_2 groups lie in one plane, with the hydrogen and boron atoms linked by two-centre two-electron bonds. The two central hydrogen atoms lie symmetrically above and below this plane, linked with the boron atoms by a three-centre two-electron bond.

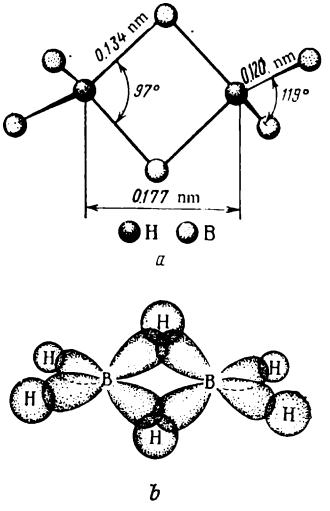


Fig. 180. B_2H_6 molecule: (*a*) structure of molecule and (*b*) overlapping of atomic orbitals

The three-centre bond arises through the overlapping of two sp^3 hybrid orbitals of boron (one from each atom) and 1*s* orbital of the hydrogen atom (Fig. 180*b*), which corresponds to the formation of bonding, nonbonding, and antibonding molecular orbitals (Fig. 181). An electron pair occupies the bonding orbital, which accounts for the stability of the B_2H_6 molecule. The effective charge on the oxygen bridge atoms is negative (0.22—) and on the boron atoms positive (0.22+).

In addition to two-centre (outer) B—H bonds and three-centre (bridge) B---H---B bonds, the B—B bonds are also displayed in the molecules of other boranes, giving rise to complex structures.

In the B_4H_{10} *tetraborane* molecule (Fig. 182) there are six B—H bonds, four three-centre B---H---B bonds and one B—B bond.

The electrons in the molecule of *pentaborane* B_5H_9 are even more delocalised and form a *five-centre bond*. Ten of the 24 electrons in the B_5H_9 molecule (Fig. 182)

are involved in the formation of five two-centre B—H bonds, eight in the formation of four three-centre B---H---B bonds, while the remaining six are involved

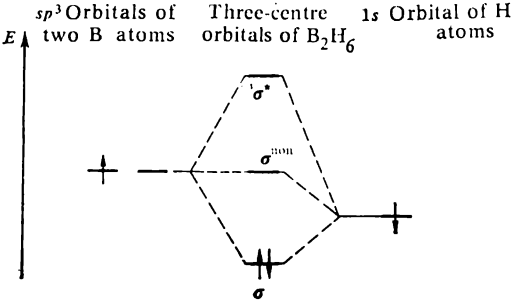


Fig. 181. Diagram of the energy levels of the three-centre orbitals of diborane B_2H_6

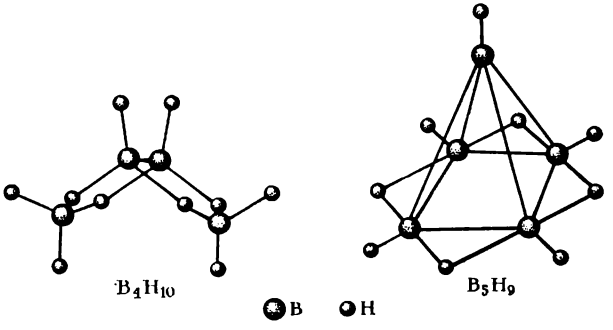
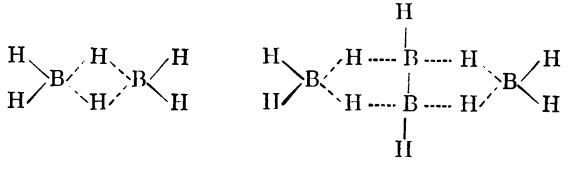


Fig. 182. Structure of tetraborane B_4H_{10} and pentaborane B_5H_9

in the construction of a five-centre bond embracing a frame of five boron atoms. Because of bond delocalisation, boron's coordination number in the pentaborane is six.

The structural formulas of the simplest boranes are as follows (three-centre bonds being designated by broken lines):



B_2H_6 B_4H_{10}

(BH_3+BH_3) $(BH_3+B_2H_4+BH_3)$

Boron hydrides are quite active (*decaborane* $B_{10}H_{14}$ is relatively less active). Most boranes ignite spontaneously in air and burn, giving

off much heat (e.g. 2025 kJ/mol for B_2H_6 against only 1425 kJ/mol for C_2H_6). This enables boranes to be used as rocket fuels.

Boron hydrides are decomposed in water, alcohols, and alkalis, with liberation of hydrogen. Diborane is hydrolised most actively:

$$B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$$

Most boranes have an offensive odour and *are very poisonous*!

In addition to the binary compounds, boron compounds of the type of $B(ClO_4)_3$, $BCl(ClO_4)_2$, and $BCl_2(ClO_4)$ have also been obtained. The first two are low-melting solids and the last a liquid. All are unstable and decompose in humid air to form acids

$$B(ClO_4)_3 + 3H_2O = H_3BO_3 + 3HClO_4$$

Being acidic, the binary compounds of boron(III) react with basic compounds to give anion complexes, for example:

$$2KOH + B_2O_3 = 2KBO_2 + H_2O$$

$$2LiH + (BH_3)_2 \xrightarrow[\text{in ether}]{} 2Li[BH_4]$$

$$NaH + BF_3 \xrightarrow[\text{in ether}]{} Na[BF_3H]$$

The compositionally simplest *anion complexes* of boron(III), *borates*, are the following: fluoborate $[BF_4]^-$, fluorohydroxyborates $[BF_3(OH)]^-$ and $[BF_2(OH)_2]^-$, fluorohydride borates $[BF_3H]^-$ and $[BF_2H_2]^-$, and borohydride $[BH_4]^-$. All correspond to sp^3 hybrid state of the boron atom and have a tetrahedral structure.

The *tetrafluoborates* are very diverse. In crystal structure and solubility they closely resemble the corresponding perchlorates. $K[BF_4]$, $Rb[BF_4]$, and $Cs[BF_4]$ are relatively insoluble, but the salts of almost all other metals are readily soluble in water.

Hydrogen fluoborate HBF_4 has not been obtained. Its aqueous solution is a strong acid prepared by dissolving H_3BO_3 in hydrofluoric acid

$$H_3BO_3 + 4HF = OH_3^+ + BF_4^- + 2H_2O$$

Tetrafluoboric acid is formed together with orthoboric acid during the hydrolysis of boron trifluoride:

$$BF_3 + 3H_2O = H_3BO_3 + 3HF$$

$$3HF + 3BF_3 + 3H_2O = 3OH_3^+ + 3BF_4^-$$

$$4BF_3 + 6H_2O = 3OH_3^+ + 3BF_4^- + H_3BO_3$$

Minute quantities of the $[BF_3OH]^-$ and $[BF_2(OH)_2]^-$ ions are formed simultaneously, as the products of partial hydrolysis

$$BF_4^- + HOH = [BF_3(OH)]^- + HF, \quad K = 2.3 \times 10^{-3}$$

Borohydrides are known for many metals. The tetrahydroborates of the alkali and alkaline-earth metals are mostly ionic compounds,

i.e. typical salts. In the solid state they are quite stable (decomposing at 250 °C to 500 °C); $Na[BH_4]$, a colourless salt readily soluble in water, is the one most commonly used. In normal conditions it is hydrolysed very slowly.

Borohydrides of the alkali metals can be prepared by the interaction of the corresponding hydride and diborane in an ether solution (see above); $Na[BH_4]$ is usually obtained by the reaction between sodium hydride and methyl orthoborate:

$$4NaH + B(OCH_3)_3 = Na[BH_4] + 3CH_3ONa$$

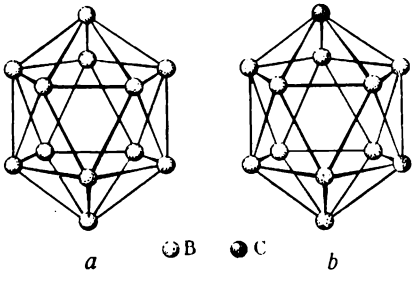
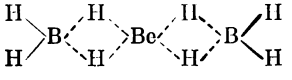


Fig. 183. Structure (*a*) of the $B_{12}H_{12}^{2-}$ ion and (*b*) $B_{10}C_2H_{12}$ molecule. The hydrogen atoms are not shown

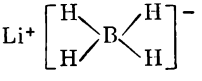
Tetrahydroborates of other metals are prepared by an exchange reaction between $Na[BH_4]$ and the corresponding halide, for example,

$$3Na[BH_4] + AlCl_3 = Al(BH_4)_3 + 3NaCl$$

Unlike the ionic tetrahydroborates, the covalent ones of the type of $Al(BH_4)_3$ (f.p. −64.5 °C, b.p. +44.5 °C), $Be(BH_4)_2$ (sublimes at 91 °C) are volatile and low-melting. They are electron-deficient compounds; the linkage between the outer and inner spheres is effected through three-centre bonds. So they are *mixed* hydrides. The electron deficit in the borohydrides of the alkali and alkaline earth metals (low ionisation energy) is eliminated by the transfer of an electron from the metal atom to the BH_4 radical, the bond between the inner and outer spheres so becoming predominantly ionic:



$Be[BH_4]_2$



$Li[BH_4]$

The most important borohydride, $Na[BH_4]$, is a white crystalline solid. The salt is quite stable and can be recrystallised from an aqueous solution. Unlike ionic borohydrides, covalent ones (*mixed* hydrides) are as reactive as the hydrides of boron, so that they explode in air.

Borohydrides are strong reductants, and are widely used in various syntheses, and as the initial compounds in the making of various hydrides, diborane in particular:

$$3NaBH_4 + 4BF_3 = 2B_2H_6 + 3NaBF_4$$

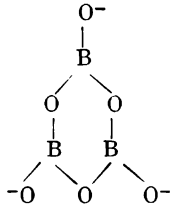
The reaction (in an ether medium) can be regarded as the displacement of one acidic compound $(BH_3)_2$ by another (BF_3).

Apart from the tetrahydroborates, various hydroborates of more complicated composition and structure are known, e.g. hydroborates of the alkali metals containing complex ions ($B_3H_8^-$, $B_{11}H_{14}^-$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$). The last ion has an icosahedral configuration with the boron atoms at the apexes (Fig. 183*a*).

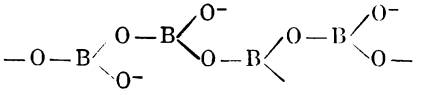
Halogen-substituted hydroborate anions, for example of the type of $[B_{10}H_{10-n}Hal_n]^{2-}$ and $[B_{12}H_{12-n}Hal_n]^{2-}$ up to $[B_{10}Hal_{10}]^{2-}$ and $[B_{12}Hal_{12}]^{2-}$ (in which Hal is Cl, Br, or I), are also quite varied.

The chemistry of boron has been recently supplemented with a new class of compounds, called *carboranes*. One of them, *barene* ($B_{10}C_2H_{12}$), is a crystalline solid (m.p. 300 °C), whose molecule has an icosahedral structure in which the carbon atoms are analogous to the boron atoms and are involved in the formation of three-centre bonds with neighbouring boron atoms (Fig. 183*b*). Barene is soluble in organic solvents. Its nucleus is very resistant to oxidants and alkalis, while the hydrogen atoms, on the contrary, are easily substituted. Numerous derivatives of carboranes, including polymeric ones, have been obtained, many with valuable physico-chemical and physico-mechanical properties (high thermal stability, mechanical strength, high dielectric strength, etc.). Their chemistry is now being intensely studied.

Like boron oxide, the *oxyborate* complexes are predominantly polymers. As the simplest one we can take the cyclic metaborate anion $(BO_2)_3^{3-}$ (in crystals of KBO_2, $NaBO_2$) and the polymetaborate anion $(BO_2)_n^{n-}$ (in the form of endless flat zig-zag chains in crystals of $Ca(BO_2)_2$, $LiBO_2$):



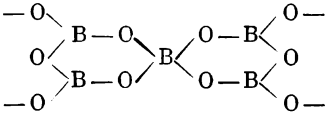
$(BO_2)_3^{3-}$



$(BO_2)_n^{n-}$

These anions consist of flat triangular BO_3 unit cells corresponding to sp^2 hybrid state of the boron atoms.

The boron atoms in oxyborates may also be in a state of sp^3 hybridisation, i.e. form four σ bonds



The modes of combination of the BO_3 triangles, BO_4 tetrahedra, and of the two together, are most varied. In hydrated oxyborates, OH groups are also coordinated around the boron atoms, all of which explains the very great variety of their composition and structure.

The phase diagram in Fig. 184 illustrates the great variety of anhydrous oxyborates.

Most oxyborates are insoluble in water, exceptions being the borates of Group I *s* elements. Sodium tetraborate $Na_2B_4O_7$ is used more than the others.

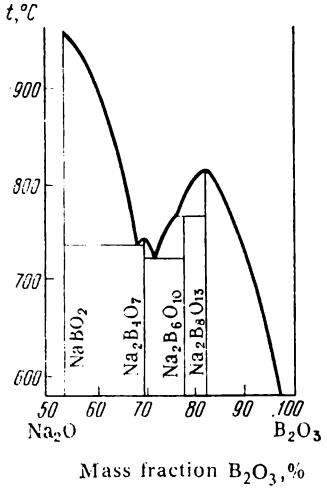
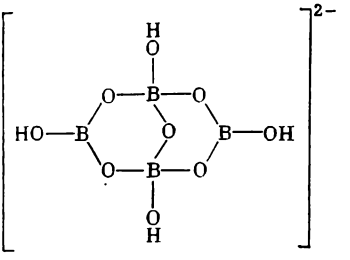


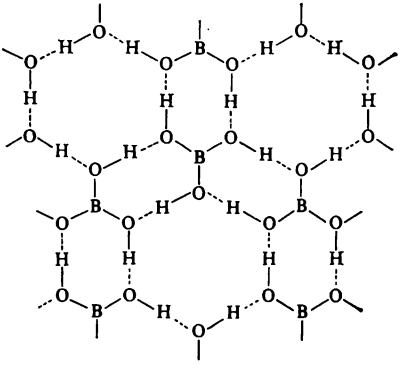
Fig. 184. Phase diagram of $Na_2O—B_2O_3$ system

The crystals of borax $Na_2B_4O_7 \cdot 10H_2O$ or $Na_2[B_4O_5(OH)_4] \cdot 8H_2O$ consist of $[B_4O_5(OH)_4]^{2-}$ anions



combined in chains by hydrogen bonding. The sodium ions Na^+ and water molecules H_2O are located between the chains and in turn link them together by means both of electrostatic forces and hydrogen bonding.

Hydrogen oxyborates are white crystalline substances. Hydrogen orthoborate (in solution *orthoboric acid*) has a layer lattice in which the H_3BO_3 molecules are linked in flat layers by hydrogen bonds, while the layers themselves are linked (at a distance of 0.318 nm) by intermolecular forces. In the solid state, therefore, H_3BO_3 consists of flakes, slippery to the touch. The structure of a layer of the H_3BO_3 crystal is as follows



Hydrogen oxyborate is relatively insoluble in water. Orthoboric acid is a very weak monobasic acid. In contrast to ordinary acids, its acidic properties are due to attachment of the OH^- ion rather than elimination of the proton:

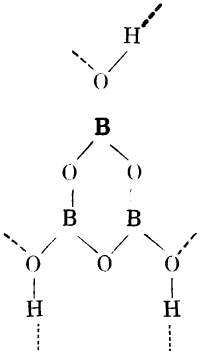
$$B(OH)_3 + HOH \rightleftharpoons [B(OH)_4]^- + H^+, \quad pK = 9.0$$

Orthoboric acid is prepared by hydrolysis of halides, boranes, etc.

When heated, hydrogen orthoborate loses water and is converted into polymeric hydrogen metaborates HBO_2 and then into B_2O_3

$$H_3BO_3 \underset{H_2O}{\overset{\text{heating}}{\rightleftharpoons}} HBO_2 \underset{H_2O}{\overset{\text{heating}}{\rightleftharpoons}} B_2O_3$$

One form of HBO_2 (m.p. 176 °C) contains cyclic $(HBO_2)_3$ unit cells combined in flat layers by hydrogen bonds:



A form of HBO_2 thermodynamically stable at room temperature (m.p. 236 °C) has a framework structure in which the boron atoms are surrounded by oxygen atoms in BO_4 tetrahedra (Fig. 185).

Since hydrogen polyborates are easily hydrated in solution, orthoboric acid is usually liberated when acids react with polyborates: e.g.

$$Na_2B_4O_7 + H_2SO_4 = Na_2SO_4 + H_2B_4O_7$$
$$H_2B_4O_7 + 5H_2O = 4H_3BO_3\downarrow$$

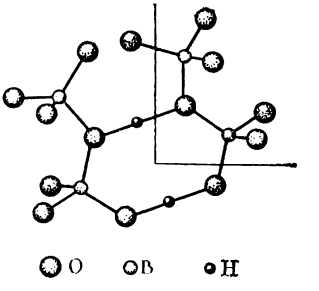


Fig. 185. A fragment of the structure of HBO_2

During the neutralisation of H_3BO_3 with excess alkali (i.e. during liberation of water), on the contrary, the B—O—B bonds characteristic of boron are restored and polyborates again formed and precipitated from the solutions as crystalline hydrates: for example,

$$4H_3BO_3 + 2NaOH + 3H_2O = Na_2B_4O_7 \cdot 10H_2O$$

Anhydrous oxyborates are obtained by fusing B_2O_3 or H_3BO_3 with the oxides of metals

$$CaO + B_2O_3 = Ca(BO_2)_2$$

Like silicates(IV) and phosphates(V), polyborates are readily vitrified.

Thus, when borax is calcined with salts of certain metals, double high-molecular polymetaborates are produced. The glasses often have a characteristic colour. $NaBO_2 \cdot Cr(BO_2)_3$, for example, is green and $2NaBO_2 \cdot Co(BO_2)_2$ blue:

$$Na_2B_4O_7 + CoO = 2NaBO_2 \cdot Co(BO_2)_2$$

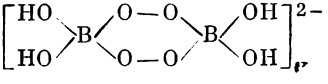
The capacity of borax to dissolve the oxides of metals is utilised in the making of enamels, for soldering metals, and in analytical chemistry to identify certain *d* elements.

The addition of $Na_2B_4O_7$ or H_3BO_3 (to between 3 and 12 per cent B_2O_3) gives silicate glass increased thermal and chemical resistance. Borosilicate glasses (*Pyrex*—SiO_2 81 per cent, ($Al_2O_3 + Fe_2O_3$) 2 per cent, B_2O_3 12 per cent, CaO 0.5 per cent, Na_2O 4.5 per cent; *Jena glass*—SiO_2 76 per cent, ($Al_2O_3 + Fe_2O_3$) 5 per cent, B_2O_3 7 per cent, CaO 1 per cent, BaO 4 per cent, Na_2O 6 per cent, K_2O 1 per cent, and others) are widely used to make chemical glassware, piping for the chemical industry, etc. Borosilicate glasses have BO_3 and BO_4 groups incorporated into the silicate lattice.

Sulphide borates(III) are obtained by fusing sulphides of metals with B_2S_3. Hydrogen sulphoborates (thioboric acids) are unstable and readily decompose in aqueous solutions

$$Ca(BS_2)_2 + H_2SO_4 = CaSO_4 + 2HBS_2$$
$$HBS_2 + 3H_2O = H_3BO_3 + 2H_2S$$

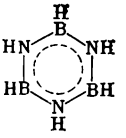
The *peroxyborates* are most varied. The simplest examples are NH_4BO_3, KBO_3, NaH_2BO_6 and $NaBO_3 \cdot 4H_2O$. Their structure has not been adequately studied; some (e.g. $NaBO_3 \cdot 4H_2O$) incorporate the $[B_2(O_2)_2(OH)_4]^{2-}$ anions with two peroxy bridge groups linking the tetrahedral atoms of boron in their crystals



Perborates are obtained either by the action of H_2O_2 on borates or of the peroxides of alkali metals on H_3BO_3. They are strong oxidants and are employed as bleaching agents in washing powders since they liberate H_2O_2 during hydrolysis.

Much attention is now being paid to organoboron compounds, in particular to those containing B—O—B, B—N—B, B—P—B, and B—S—B chains surrounded by organic radicals. The derivatives of

borazole $B_3N_3H_6$ present special interest

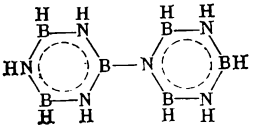


Borazole is a colourless liquid (m.p. —58 °C, b.p. 55 °C). It is similar to benzene in structure and certain properties and is therefore often called 'inorganic benzene'.

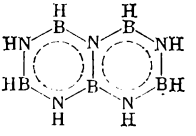
The presence of a nonlocalised π bond (as in benzene) accounts for the shorter internuclear distance d_{BN} in borazole (0.144 nm as compared with a normal B—N bond length of 0.154 nm). The distribution of electron density corresponds to $N^{\delta-}—B^{\delta+}$ and opposite polarity of the $N^{\delta-}—H^{\delta+}$ and $B^{\delta+}—H^{\delta-}$ bonds. The reactivity of borazole is high, exceeding that of benzene. It decomposes in air when heated, in water and in the presence of acids. It can be prepared by heating lithium tetrahydroborate and ammonium chloride:

$$3LiBH_4 + NH_4Cl = B_3N_3H_6 + 3LiCl + 9H_2$$

Among the products of borazole conversion that have been isolated are an analogue of diphenyl



and an analogue of naphthalene



Both borazole itself and its derivatives present practical as well as theoretical interest. There are, for example, oil-resistant and thermally stable organoboron compounds. Borazole derivatives have also found application as rocket fuels.

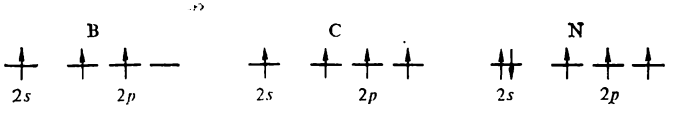
It will be clear from the foregoing that boron compounds with nitrogen resemble carbon compounds in many respects. We have observed this analogy in our examples of the two forms of boron nitride (graphite-like and diamond-like) and of borazole and its derivatives. The illustration can be continued in the following

examples:

$H_3C—CH_3$	$H_2C=CH_2$	$HC\equiv CH$
Ethane	Ethylene	Acetylene
$H_3N—BH_3$	$H_2N=BH_2$	$HN\equiv BN$
Borazane	Borazene	Borazine

In all these compounds, tetravalent atoms of boron and nitrogen imitate the structure of carbon; the fourth B—N bond arises through an sp^3 hybrid nonbonding electron pair of nitrogen and a free sp^3 hybrid orbital of the boron atom.

In relatively simple derivatives, the carbon-atom structure is imitated by the boron and nitrogen atoms through the formation of anion and cation complexes respectively that are isoelectronic with the corresponding carbon compounds: for example,



BH_4^-	CH_4	NH_4^+
BF_4^-	CF_4	NF_4^+
$B_2H_6^{2-}$	C_2H_6	$N_2H_6^{2+}$

7.2. Aluminium

The aluminium atom ($1s^22s^22p^63s^23p^1$) is larger than the boron one and has a lower ionisation energy, therefore its nonmetallic character is less pronounced than boron's. Its most characteristic oxidation state (like boron) is +3. A negative polarisation is even less frequent than with boron. The most characteristic coordination numbers of aluminium(III) are six and four.

Coordination number of Al(III)	Spatial arrangement of ligands	Typical compounds
4	tetrahedral	$AlCl_4^-$, AlH_4^-, Al_2Hal_6, aluminosilicates
6	octahedral	Al_2O_3, AlF_6^{3-}, AlF_3, $AlCl_3$ (c), $[Al(OH_2)_6]^{3+}$, $[Al(OH)_4(OH_2)_2]^-$

Aluminium is a typical amphoteric element. Unlike boron, both cation and anion complexes are typical of it.

Aluminium is the fourth element in abundance in the Earth's crust (6.6 mole per cent), after O, H, and Si. It consists of one stable isotope, ^{27}Al. Most of it is concentrated in *aluminosilicates*. Other minerals of greatest industrial importance are *bauxite* $Al_2O_3 \cdot nH_2O$ and *cryolite* Na_3AlF_6. A common product of the breakdown of rocks,

kaolin, consists mainly of the clay mineral *kaolinite* $Al_4[Si_4O_{10}](OH)_8$ ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$).

The simple substance. Aluminium is a silvery white metal (m.p. 660 °C, b.p. about 2500 °C). It crystallises with a face centred cubic lattice, has high electrical and thermal conductivity, and is exceptionally plastic.

Aluminium is chemically active; even in normal conditions it becomes covered with a very strong, extremely thin (0.00001 mm) film of oxide that dulls its metallic lustre slightly but is responsible for its quite high corrosion resistance. Aluminium burns in oxygen only at high temperatures and then only in a finely powdered state. The interaction is accompanied with the liberation of much heat (ΔH° = = — 1676 kJ/mol Al_2O_3). It reacts with sulphur in a similar way, chlorine and bromine at ordinary temperatures, and with iodine after heating or in the presence of water, which acts as a catalyst in this reaction. When strongly heated, aluminium reacts with nitrogen (800 °C) and carbon (2000 °C). It does not react directly with hydrogen.

Because of its high affinity for oxygen (ΔG° = — 1582 kJ/mol Al_2O_3), aluminium actively reduces many metals from their oxides (*aluminothermy*). The reaction is usually accompanied with the liberation of much heat, and the temperature rises to between 1200 °C and 3000 °C. The process is employed to produce manganese, chromium, vanadium, tungsten, and iron alloys.

Aluminium's high chemical (reducing) activity is also shown by its standard electrode potential in acidic and alkaline media:

$$Al^{3+} + 3e^- = Al, \qquad E^\circ_{298} = -1.66 \text{ V}$$

$$AlO_2^- + 2H_2O + 3e^- = Al + 4OH^-, \qquad E^\circ_{298} = -2.35 \text{ V}$$

Being amphoteric, aluminium dissolves in acidic and alkali solutions to form cation and anion complexes respectively

$$2Al + 6OH_3^+ + 6H_2O = 3H_2 + 2[Al(OH_2)_6]^{3+}$$

$$2Al + 6H_2O + 6OH^- = 3H_2 + 2[Al(OH)_6]^{3-}$$

In both cases, its oxidation is accompanied with liberation of hydrogen. When the oxide film is removed from its surfaces (mechanically or by amalgamation), aluminium reacts energetically with water:

$$2Al + 6H_2O = 2Al(OH)_3 + 3H_2$$

Because of the protective effect of the oxide film, aluminium is table under the action of very dilute HNO_3, and of concentrated HNO_3 and H_2SO_4 in the cold. Its tendency to passivation makes it possible to improve its corrosion resistance by treating its surface with suitable oxidants (concentrated HNO_3, $K_2Cr_2O_7$) or by anode oxidation, by which the oxide film can be made thicker. Aluminium's

stability is the reason for its use in containers to store and handle nitric acid.

Aluminium is one of the most widely used metals, being used in the manufacture of chemical apparatus, electrical conductors, capacitors, etc. Aluminium foil (0.005 mm thick) is used for packaging foods and drugs. The bulk of aluminium is used, however, to make light alloys, viz., *duralumin* (Al 94 per cent, Cu 4 per cent, and 0.5 per cent each of Mg, Mn, Fe and Si), *silumin* (Al 85-90 per cent, Si 10-14 per cent, Na 0.1 per cent), etc. Aluminium alloys are widely used in building of motor vehicles, ships and river vessels, aircraft, etc. It is also used as an alloying additive in many alloys, giving them thermal resistance. Its compounds with *d* elements (*aluminides*) and their alloys (NiAl, Ni_3Al, CoAl, Ti_3Al, TiAl, etc.) are used as heat resistant materials (to temperatures up to 1200 °C).

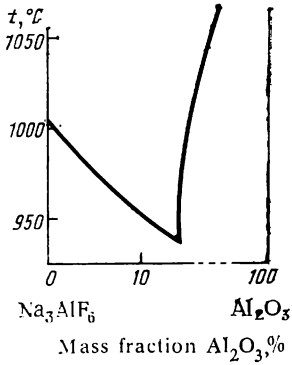


Fig. 186. A fragment of the phase diagram of an Na_3AlF_6—Al_2O_3 system

In industry aluminium is obtained by electrolysis of a solution of alumina Al_2O_3 in molten cryolite Na_3AlF_6. A concentration of 92 to 94 per cent of Na_3AlF_6 in its mixture with Al_2O_3 corresponds to the eutectic composition (Fig. 186). The process can therefore be carried out at comparatively low temperatures (800 °C to 1000 °C). Liquid aluminium is liberated at the walls of the electrolytic bath, which serves as the cathode and oxygen at the carbon anode. Oxygen reacts with the carbon anode. Since the density of the melt is relatively low, the aluminium is precipitated to the bottom of the bath.

Compounds of aluminium(III). In normal conditions the binary compounds of aluminium(III) are polymeric white solids.

Aluminium *oxide* is known in several forms. The stablest crystalline form is α-Al_2O_3 (rhombic lattice). Its crystals have an octahedral-tetrahedral coordination of the atoms, the coordination number of Al being six and of O four (see Fig. 72). This form occurs in the crust as the mineral *corundum*, which often contains admixtures that colour it. Transparent coloured crystals of corundum, viz., ruby (red owing to the presence of Cr^{3+}) and sapphire (blue owing to Ti^{4+}, Fe^{2+} and Fe^{3+}) are gem stones. They can also be produced artificially.

The high strength of the Al—O—Al bonds and dense crystal structure of aluminium oxide account for its high enthalpy of formation and melting point (about 2050 °C), and great hardness and refractoriness. Corundum, for example, is comparable with diamond (and

carborundum and borazon) in hardness and is used as an abrasive. Al_2O_3, trade mark abrasite *Alundum*, produced artificially from bauxite by fusing, is also used as a refractory and abrasive. Artificially produced single crystals of corundum (especially rubies) are used as bearings in precision mechanisms because of their great hardness. Artificial rubies are now also used as quantum generators (lasers).

The crystalline modifications of Al_2O_3 are very stable chemically, not reacting either with acids or with water. Alkalis destroy them only after prolonged heating.

The main field of application of Al_2O_3 is in the production of metallic aluminium. The *alumina* employed for the purpose is obtained from bauxite, and by complex treatment from nepheline.

Aluminium *hydroxide* $Al(OH)_3$ is a polymeric compound. The natural hydroxide (the mineral *hydrargillite*) for instance, has a layer crystal lattice (Fig. 187) consisting of $Al(OH)_6$ octahedra. The layers are linked together by hydrogen bonds. The hydroxide obtained by an exchange reaction is a gelatinous white precipitate, whose composition and structure largely depend on the reaction and storage conditions. The commonly used equation for obtaining the hydroxide

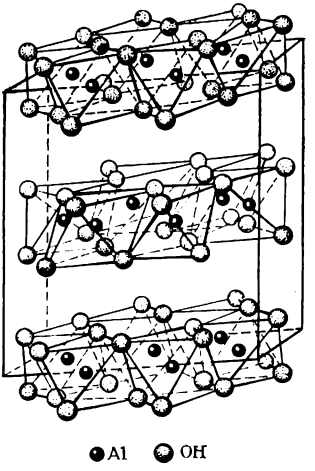


Fig. 187. Structure of hydrargillite $Al(OH)_3$

$$Al^{3+} + 3OH^- = Al(OH)_3\downarrow$$

does not reveal the complexity of the mechanism of its formation. It would better be represented as follows. The water molecules are gradually replaced by OH^- ions in aquo complexes $[Al(OH_2)_6]^{3+}$ during their reaction with alkali:

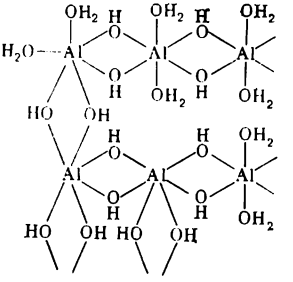
$$[Al(OH_2)_6]^{3+} + OH^- = [Al(OH)(OH_2)_5]^{2+} + H_2O$$

$$[Al(OH)(OH_2)_5]^{2+} + OH^- = [Al(OH_2)(OH_2)_4]^{+} + H_2O$$

$$[Al(OH)_2(OH_2)_4]^{+} + OH^- = [Al(OH)_3(OH_2)_3]^{0} + H_2O$$

At the same time polymerisation takes place with the formation of polynuclear complexes; finally a precipitate with a variable $Al_2O_3 \times$

× nH_2O composition is liberated



The precipitate is gradually converted on standing into crystalline $Al(OH)_3$ (with liberation of water), and becomes unreactive ('ages'). Crystalline $Al(OH)_3$ is prepared by passing CO_2 into an alkaline solution of aluminate.

When $Al_2O_3 \cdot nH_2O$ is calcined, it gradually loses its water and is converted into oxol derivatives, and finally into Al_2O_3. The dehydration mechanism is quite complicated, and the intermediates obtained have various properties, depending on the dehydration conditions and the initial substances. Some are chemically active (with a prevalence of OH bridges) and are readily soluble in acids and alkalis, while others are chemically inactive (the OH groups being replaced by oxygen atoms) and only react by fusing with alkalis. One form of dehydrated aluminium hydroxide, *alumina gel*, is used in industry (like silica gel) as an adsorbent.

Aluminium hydroxide is a typical amphoteric compound and when fresh is readily soluble in alkalis and acids, the high-molecular hydroxide being broken down, producing either complex cations or complex anions, depending on the medium:

$$[Al(OH_2)_6]^{3+} \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} Al(OH)_3 \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} [Al(OH)_6]^{3-}$$

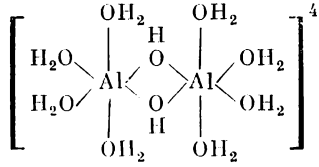
Crystal hydrates of the corresponding salts of aluminium are precipitated from acid solutions, e.g. $AlCl_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $\overset{+1}{M}Al(SO_4)_2 \cdot 12H_2O$ (alum). The salts of aluminium and oxygen-containing acids are soluble in water, but $AlPO_4$, which has a coordination lattice of SiO_2 type, is insoluble.

Aluminium salts are hydrolysed in solution. The initial stages of the hydrolysis can be described by the following equations:

$$[Al(OH_2)_6]^{3+} + H_2O \rightleftarrows [Al(OH)(OH_2)_5]^{2+} + OH_3^+, \quad K = 1.12 \times 10^{-5}$$

$$[Al(OH)(OH_2)_5]^{2+} + H_2O \rightleftarrows [Al(OH)_2(OH_2)_4]^{+} + OH_3^+$$

$$2[Al(OH_2)_6]^{3+} + 2H_2O \rightleftarrows$$

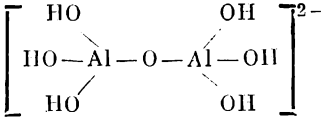


$$+ 2OH_3^+$$

The sulphide, carbonate, cyanide, and certain other salts of aluminium are unobtainable from aqueous solutions because of hydrolysis.

Commonly used aluminium salts are the sulphate and the alums, which are used in paper-making (as in sizing writing paper), in tanneries for leather tanning, in the textile industry for dyeing fabrics, etc.

Some aluminates, when crystallised from alkaline solutions, retain the composition of the hydroxy compounds (e.g. $Ca_3[Al(OH)_6]_2$) while others are partly dehydrated to form, e.g. $K_2[Al_2O(OH)_6]$:



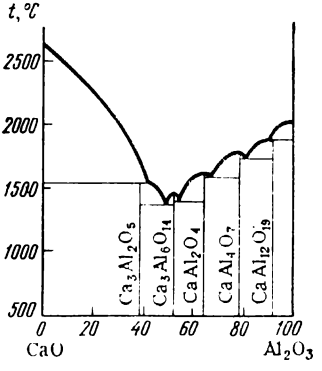


Fig. 188. Phase diagram of a $CaO-Al_2O_3$ system

By fusing $Al(OH)_3$ or Al_2O_3 with alkalis, high-molecular metaoxyaluminates are obtained. Their composition is quite varied, as will be seen from Fig. 188. The oxyaluminates of alkali metals are easily hydrolysed (to precipitation of $Al(OH)_3$).

The unit cell of meta-oxyaluminates (as of aluminium oxide) is an AlO_6 octahedron. Certain mixed oxides, e.g. *spinel* $MgAl_2O_4$ (see p. 265), and the aluminates of a $\overset{+2}{M}Al_2O_4$ or $\overset{+2}{M}(AlO_2)_2$ type (where M is Be, Zn, Fe, or Mn), which are similar to spinel in composition and structure, can also be regarded as meta-aluminates.

The capacity of aluminium to yield anion complexes explains its natural occurrence in the form of aluminosilicates, in which it plays the same role as silicon; both elements form a mixed compound, aluminate-silicate. Aluminosilicates can be regarded as silicates in which some oxysilicon tetrahedra SiO_4^{4-} are replaced by oxyalumini-

um tetrahedra AlO_4^{5-}. Partial substitution of Si atoms for Al in SiO_2 (or Si_4O_8) gives aluminosilicate ions of a $[AlSi_3O_8]^-$ and $[Al_2Si_2O_8]^{2-}$ type. When the Si atoms in silicate ions $Si_2O_5^{2-}$ (or $Si_4O_{10}^{4-}$) with a layer structure are replaced by Al atoms, layer aluminosilicate ions are formed, e.g. $[AlSi_3O_{10}]^{5-}$.

Most common aluminosilicates are *felspars*. Their main representatives are *orthoclase* $K[AlSi_3O_{10}]$, *albite* $Na[AlSi_3O_{10}]$, and *anorthite* $Ca[Al_2Si_2O_{10}]$. Minerals of the *mica* group, e.g. *muscovite* $KAl_2[AlSi_3O_{10}](OH)_2$, are also very common.

The mineral *nepheline* $(Na,K)_2[Al_2Si_2O_8]$ is of great practical importance.

Nepheline is used to obtain alumina, soda products, and cement. The production process comprises the following operations:

(a) nepheline and limestone are fused in tube furnaces at 1200 °C

$$(Na,K)[Al_2Si_2O_8] + 2CaCO_3 = 2CaSiO_3 + NaAlO_2 + KAlO_2 + 2CO_2\uparrow$$

(b) the mass formed is leached with water, forming a solution of aluminates of sodium and potassium, and a sludge $CaSiO_3$:

$$NaAlO_2 + KAlO_2 + 4H_2O = Na[Al(OH)_4] + K[Al(OH)_4]$$

(c) the CO_2, formed during the fusion process, is passed into the solution of aluminates:

$$Na[Al(OH)_4] + K[Al(OH)_4] + 2CO_2 = NaHCO_3 + KHCO_3 + 2Al(OH)_3$$

(d) alumina is obtained by heating $Al(OH)_3$:

$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

(e) the mother liquor is evaporated to precipitate soda and potash, while the $CaSiO_3$ sludge obtained earlier is used in the production of cement.

The production of one tonne of Al_2O_3 yields one tonne of soda products and 7.5 tonnes of cement. Complex treatment of cheap nepheline thus yields valuable products like alumina, soda (potash), and cement.

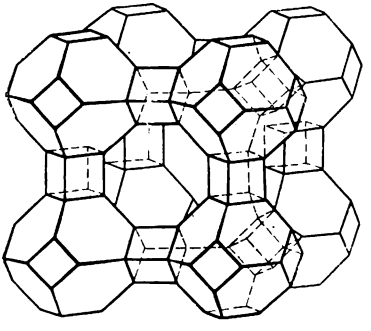


Fig. 189. Structure of a zeolite

Other aluminosilicates of great practical importance are *zeolites*. Their composition can be expressed by the formula $M_xE_yO_{2y}\cdot nH_2O$ where M is Ca or Na (less often Ba, Sr, K), and E is Si and Al in various proportions. Figure 189 shows a model of an artificial zeolite. Oxysilicon and oxyaluminium tetrahedra are united in polyhedra linked by oxygen atoms. Because of this structure, zeolite crystals have free cavities of definite size.

The M^+ and M^{2+} ions located in these cavities offset the negative charge of the oxy-alumino-silicon tetrahedra, and water molecules

can therefore enter them. The water-absorbing capacity depends on the water vapour pressure. Zeolites can exchange water for other substances (alcohol, ammonia, etc.) and when carefully heated, the water is gradually removed; even complete dehydration does not destroy their crystalline lattice.

Artificial zeolites are used as *molecular sieves*, that absorb substances whose molecules can pass into their cavities (0.3-1.3 nm in diameter). A molecular sieve (with 0.35 nm openings) can absorb molecules of H_2, O_2, and N_2 but not the larger molecules of CH_4 or atoms of Ar. Molecular sieves are used to separate hydrocarbons and dry gases and liquids.

Some cations can be substituted for others in zeolites, which is the basis for their use as ion exchangers (cation exchanger). Zeolites incorporating ions of certain *d* elements are catalysts.

Aluminium *sulphide* Al_2S_3 is obtained by direct reaction between the simple substances (at red heat). It is a crystalline solid (m.p. 1100 °C) that is hydrolysed completely even by traces of moisture in the air. When Al_2S_3 is fused with basic sulphides, polymeric sulphide aluminates $\overset{+1}{M}Al\overset{+3}{S}_2$ and $\overset{+2}{M}(Al\overset{+3}{S}_2)_2$ are formed. They are unstable and easily decomposed in water.

The *halides* of aluminium $AlHal_3$ are colourless crystalline solids in normal conditions. They can be prepared by direct interaction of the simple substances, but the main method of obtaining AlF_3 is based on the action of anhydrous HF on Al_2O_3 or Al:

$$Al_2O_3 + 6HF = 2AlF_3 + 3H_2O$$

while $AlCl_3$ is prepared by chlorinating Al_2O_3 in the presence of coal (at 500 °C to 550 °C).

	AlF_3	$AlCl_3$	$AlBr_3$	AlI_3
M. p., °C	1290	193	97.5	179.5
B. p., °C	1291 (subl.)	180 (subl.)	255	381
Density, g/cm³	3.1	2.5	3.2	4.0
$\Delta H^\circ_{f,\,298}$, kJ/mol	—1510	—705	—513	—308
$\Delta G^\circ_{f,\,298}$, kJ/mol	—1432	—629	—491	—304

Aluminium fluoride differs markedly in properties from the other halides, having a coordination lattice of the ReO_3 type (see Fig. 71), and being high-melting, insoluble in water, and unreactive. The chloride has a layer lattice, while the crystals of $AlBr_3$ and AlI_3 consist of dimeric Al_2Hal_6 molecules (Fig. 190) and are therefore low-melting, quite volatile at normal temperatures, very hygroscopic and deliquescent in air. They are readily soluble in many organic solvents, as well as in water.

In the vapourous state, and in certain organic solvents, $AlCl_3$, $AlBr_3$, and AlI_3 are in the form of dimeric Al_2Hal_6 molecules with

a twinned tetrahedral configuration with a common edge (Fig. 190). Simple molecules of $AlHal_3$ exist only at high temperatures; Al_2Cl_6, for example, dissociates into $AlCl_3$ molecules at 700 °C.

Unlike the typical salts, aluminium halides (except AlF_3) are very reactive. Their interaction with water liberates considerable

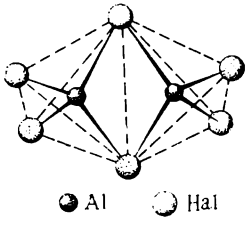


Fig. 190. Structure of the molecule of Al_2Hal_6

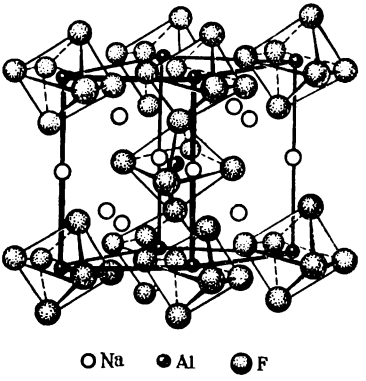
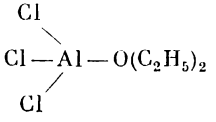


Fig. 191. Structure of cryolite Na_3AlF_6

heat. They are strongly hydrolysed, but in contrast to the typical acidic halides of nonmetals, the hydrolysis is incomplete and reversible.

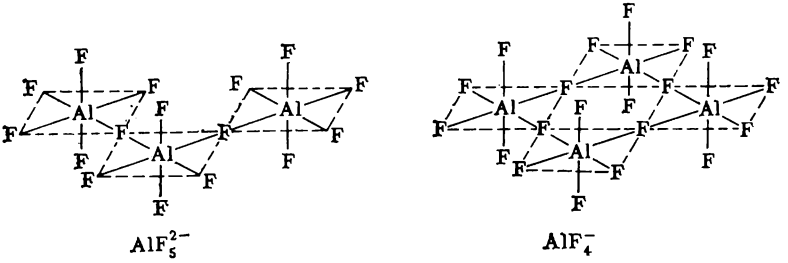
Like $BHal_3$, aluminium trihalides (except AlF_3) are strong acceptors of electron pairs, and attach donor-molecules: for example,



$AlHal_3$ have a tendency to complexation in relation to H_2O, H_3N, PCl_5, $POCl_3$, and certain organic compounds, which explains the use of $AlCl_3$ as a catalyst in organic synthesis.

With basic halides, $AlHal_3$ readily form halogen aluminates of the type of $\overset{+1}{M}_3AlF_6$, $\overset{+1}{M}_2AlF_5$, and $\overset{+1}{M}AlHal_4$, of which sodium hexafluoroaluminate Na_3AlF_6 (*cryolite*) is the most stable. Cryolite crystals of an insular type are formed by the ions Na^+ and AlF_6^{3-} (Fig. 191). Fluoroaluminates of $\overset{+1}{M}_2AlF_5$ and $\overset{+1}{M}AlF_4$ composition are formed by polymeric fluoroaluminate complexes; in the Tl_2AlF_5 crystal, for instance, the AlF_6 octahedra are united at two common apexes (F atoms) into endless chains of an AlF_5^{2-} composition, while in $KAlF_4$, the AlF_6 octahedra (united at four apexes) form an endless

AlF_4^- anion in the form of network



AlF_5^{2-} AlF_4^-

The joining of AlF_6 octahedra at all six apexes yields an AlF_3 coordination crystal lattice (see above).

The fluoroaluminates of the alkali metals are poorly soluble in water. That most used is Na_3AlF_6 (to produce Al, F_2, enamels, glass, etc.). Industrial production of artificial cryolite is based on treating aluminium hydroxide with hydrofluoric acid and soda:

$$2Al(OH)_3 + 12HF + 3Na_2CO_3 = 2Na_3AlF_6 + 3CO_2 + 9H_2O$$

The coordination number of aluminium in chloro-, bromo-, and iodo-aluminates is four. These substances are obtained by fusing aluminium trihalides with a corresponding metal halide (see Fig. 133). Derivatives of the alkali metals, e.g. $Na[AlCl_4]$ (m.p. 156 °C), $Cs[AlCl_4]$ (m.p. 377 °C) are typical salts. In contrast to the fluoroaluminate ion, the $[AlCl_4]^-$, $[AlBr_4]^-$ and $[AlI_4]^-$ ions are easily hydrolysed, so that the corresponding salts are soluble in water.

Aluminium forms a polymeric *hydride* AlH_3 that is prepared indirectly, for example, by reacting $AlCl_3$ with ether solutions of aluminium hydrides:

$$3Li[AlH_4] + AlCl_3 = 4AlH_3 + 3LiCl$$

Aluminium hydride $(AlH_3)_n$ is a white powder decomposing at temperatures above 105 °C with liberation of hydrogen. Like boron hydrides, it is an electron-deficient compound. It presumably has a network structure, in which the aluminium atoms are surrounded by hydrogen atoms in octahedral structures, each neighbouring pair of Al atoms being connected by two three-centre two-electron bonds through hydrogen atoms above and below the plane of their network. A fragment of the structure of AlH_3 is shown in Fig. 192.

An ether solution of AlH_3 reacts with basic hydrides to form aluminium hydrides:

$$LiH + AlH_3 = Li[AlH_4]$$

Aluminium hydrides are white solids, much less stable than the corresponding boron hydrides, and vigorously decomposed by water.

They are strong reducing agents and are used in organic synthesis (especially $Li[AlH_4]$).

Aluminium borohydride $Al[BH_4]_3$ (f.p. −64.5 °C, b.p. 44.5 °C) can be regarded as a mixed hydride of boron and aluminium. It, too, is an electron-deficient compound. The boron and aluminium

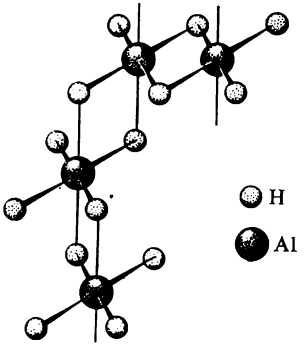


Fig. 192. A fragment of the structure of aluminium hydride $(AlH_3)_n$

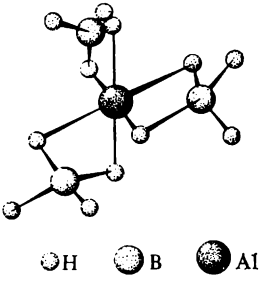


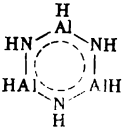
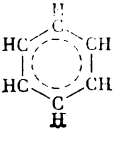
Fig. 193. Structure of $Al(BH_4)_3$

atoms are linked through hydrogen by two three-centre two-electron bonds (Fig. 193). $Al[BH_4]_3$ can be obtained by the following exchange reaction in an ether medium

$$3Na[BH_4] + AlCl_3 = Al[BH_4]_3 + 3NaCl$$

$Al[BH_4]_3$ is extremely active, and has possibilities as a rocket fuel.

Compounds similar in structure to the corresponding carbon ones are known for aluminium as well as for boron, e.g.

$H_3N—AlH_3$	$H_2N=AlH_2$	$HN\equiv AlH$	
Alazane	Alazene	Alazine	Alazole
$H_3C—CH_3$	$H_2C=CH_2$	$HC\equiv CH$	
Ethane	Ethylene	Acetylene	Benzene

These aluminium compounds are less stable than the similar boron compounds. Some are known only at low temperatures in a polymerised state.

Our survey shows that aluminium is much more metallic in character than boron. Unlike the acidic compounds of boron, similar compounds of aluminium(III) display amphoteric properties. The weakening of acidic properties in aluminium(III) derivatives compared with boron(III) and silicon(IV) can be illustrated by the following examples

$CaO\ (c) + B_2O_3\ (c) = Ca(BO_2)_2\ (c)$, $\Delta G^\circ_{298} = -126$ kJ
$CaO\ (c) + Al_2O_3\ (c) = Ca(AlO_2)_2\ (c)$, $\Delta G^\circ_{298} = -24$ kJ
$CaO\ (c) + SiO_2\ (c) = CaSiO_3\ (c)$, $\Delta G^\circ_{298} = -112$ kJ
$NaOH\ (c) + H_3BO_3\ (c) = NaBO_2\ (c) + 2H_2O\ (l)$, $\Delta G^\circ_{298} = -48$ kJ
$NaOH\ (c) + Al(OH)_3\ (c) = NaAlO_2\ (c) + 2H_2O\ (l)$, $\Delta G^\circ_{298} = -13$ kJ
$NaF\ (c) + BF_3\ (g) = NaBF_4\ (c)$, $\Delta G^\circ_{298} = -100$ kJ
$NaF\ (c) + {}^1/_3AlF_3\ (c) = {}^1/_3Na_3AlF_6\ (c)$, $\Delta G^\circ_{298} = -26$ kJ
$NaF\ (c) + {}^1/_2SiF_4\ (c) = {}^1/_2Na_2SiF_6\ (c)$, $\Delta G^\circ_{298} = -51$ kJ
$NaF\ (c) + MgF_2\ (c) = NaMgF_3\ (c)$, $\Delta G^\circ_{298} = -14$ kJ
$KH\ (c) + {}^1/_2B_2H_6\ (g) = KBH_4\ (c)$, $\Delta G^\circ_{298} = -170$ kJ
$KH\ (c) + AlH_3\ (c) = KAlH_4\ (c)$, $\Delta G^\circ_{298} = -112$ kJ
$KCl\ (c) + MgCl_2\ (c) = KMgCl_3\ (c)$, $\Delta G^\circ_{298} = -16$ kJ
$KCl\ (c) + AlCl_3\ (c) = KAlCl_4\ (c)$, $\Delta G^\circ_{298} = -114$ kJ

Analysis of ΔG values shows that the aluminium compounds (Al_2O_3, $Al(OH)_3$, AlF_3, AlH_3) are more basic in character than similar boron compounds (B_2O_3, H_3BO_3, BF_3, B_2H_6) and silicon ones (SiO_2, SiF_4), are more acidic than Mg(II) compounds.

7.3. Gallium Subgroup

The gallium subgroup comes immediately after the *d* element family in the periodic system, so that *d* contraction has a significant effect on the properties of its elements. In the transition from Al to Ga, for instance, the atomic radius is rather shorter, while the ionisation energy is higher. The properties of thallium are also affected by *f* contraction so that the size of the atom and ion increases very little in the transition from In to Tl, while the ionisation energy even rises slightly. The other properties of elements of the gallium subgroup change in the same order as in the other subgroups of *p* elements.

As with the *p* element subgroups already discussed, the involvement of s^2 electrons in the formation of bonds decreases with increasing atomic number. The $6s^2$ electron pair is especially inactive, so that, while a +3 oxidation state is most characteristic of gallium,

the most stable oxidation state of thallium is +1. The most frequent oxidation state of indium is +3.

Gallium, indium, and thallium are very dispersed elements. They form practically no independent minerals, but are found in certain polymetallic ores. Gallium often occurs together with aluminium. Natural Ga, In, and Tl consist of the following isotopes: ^{69}Ga (60.5 per cent) and ^{71}Ga (39.5 per cent); ^{113}In (4.33 per cent) and ^{115}In (95.67 per cent), and ^{205}Tl (70.50 per cent) and ^{203}Tl (29.50 per cent).

The simple substances. As simple substances gallium, indium, and thallium are silvery-white low-melting metals. Unlike other lustrous metals, indium reflects all wavelengths of light most uniformly and is therefore used to make mirrors. The most important characteristics of these metals are given in the following table:

	Ga	In	Tl
Density, g/cm^3	5.91	7.36	11.85
M. p., °C	29.8	156	304
B. p., °C	2250	2040	1470
$\Delta H^\circ_{\text{subl.},298}$, kJ/mol	262.5	234.9	169.3
S°_{298}, J/K·mol	41.1	57.82	64.18
Electrical conductivity	2	12	5
E°_{298}, V			
$E^{3+} + 3e^- \rightarrow E$	−0.53	−0.34	+0.72
$E^{+} + 1e^- \rightarrow E$	—	—	−0.34

Liquid gallium is liable to supercooling and does not set for a long time. Of all known substances, it can remain in the liquid state over the widest range of temperatures. Its low melting point, high boiling point, and tendency to supercooling make it suitable for use in thermometers for measuring high temperatures.

Like aluminium, gallium and indium become coated with a strong oxide film when exposed to air, and are therefore practically unaltered. Thallium oxidises slowly. Gallium, indium and especially thallium react vigorously with oxygen and sulphur when heated. They react with chlorine and bromine at normal temperatures, but with iodine only when heated.

In addition to its use for making high-grade mirrors, indium is employed as an electrolytic coating on other metals to protect them against corrosion.

Gallium, indium, and thallium come before hydrogen in the electromotive series. Gallium and indium dissolve in dilute acids. In accordance with its stable oxidation state, Tl reacts with acids to form Tl(I) derivatives. Gallium is passivated in hydrochloric acid through the formation of water-insoluble TlCl. Gallium, like aluminium, is soluble in alkalis:

$$2Ga + 6H_2O + 6NaOH = 3H_2 + 2Na_3[Ga(OH)_6]$$

Indium and especially thallium are stable in alkalis in the absence of strong oxidants.

Metallic gallium and its analogues are obtained by a quite complicated chemical processing of polymetallic ores. After a repeated treatment and refining, oxides and chlorides of the metals are separated from the ores. The pure metals are recovered from the oxides and chlorides by chemical or electrochemical reduction.

Gallium and its analogues are easily fused with many metals, often forming eutectic alloys with low melting points. An alloy consisting of In 18.1 per cent, Bi 41 per cent, Pb 22.1 per cent, Sn 10.6 per cent and Cd 8.2 per cent, for example, melts at a temperature as low as 47 °C; another alloy consisting of Ga 90 per cent, Sn 8 per cent and Zn 2 per cent melts at an even lower temperature of 19 °C.

Compounds of gallium(III), indium(III), and thallium(III). As with aluminium(III), the most characteristic coordination numbers of Ga(III), In(III) and Tl(III) are six, less often four. The forms of Ga_2O_3 are thus similar in structure to the corresponding forms of Al_2O_3. The coordination number of In and Tl in the crystals of In_2O_3 and Tl_2O_3 is also six.

Direct interaction of the simple substances yields white Ga_2O_3 and yellow In_2O_3. Brown Tl_2O_3 is formed indirectly from Tl(III) compounds and by oxidation Tl_2O_3 by ozone. At 100 °C Tl_2O_3 begins to lose its oxygen. The relative stability of the oxides is illustrated by their enthalpies and Gibbs' energies:

	Ga_2O_3	In_2O_3	Tl_2O_3
$\Delta H^\circ_{f,\,298}$, kJ/mol	—1088	—927	—417
$\Delta G^\circ_{f,\,298}$, kJ/mol	—996	—837	—318

The oxides are practically insoluble in water. Solubility in acids increases in the series Ga_2O_3—In_2O_3—Tl_2O_3 with increasing basic properties. For example, for reactions

$$E_2O_3\ (s) + 6HCl\ (sol) = ECl_3\ (sol) + 3H_2O\ (l)$$

the changes in the standard Gibbs' energy for Ga_2O_3, In_2O_3, and Tl_2O_3 are +71, —25, and —199 kJ/mol respectively.

The $E(OH)_3$ *hydroxides* are gelatinous precipitates of indefinite composition, insoluble in water, prepared in the same way as $Al(OH)_3$. White $Ga(OH)_3$ displays basic and acidic functions about equally. Basic properties predominate in white $In(OH)_3$, while reddish-brown $Tl(OH)_3$ has no appreciable acidic function. There is thus a distinct strengthening of basic properties and weakening of acidic ones in the $Ga(OH)_3$—$In(OH)_3$—$Tl(OH)_3$ series (like the oxide series), which accords with the increase in size of E(III) atoms.

Aquo complexes are formed when $E(OH)_3$ and E_2O_3 are dissolved in acids, e.g.

$$Ga(OH)_3 + 3OH_3^+ = [Ga(OH_2)_6]^{3+}$$

Compounds of Ga(III), In(III), and Tl(III) are therefore always separated from aqueous solutions in the form of crystal hydrates, e.g. $EHal_3 \cdot 6H_2O$, $KE(SO_4)_2 \cdot 12H_2O$ (alum). The aquo complexes of Ga(III) and In(III) are colourless and that of Tl(III) pale yellow. In general the solubility and hydrolysis of Ga(III) and In(III) compounds is the same as those of the corresponding aluminium compounds.

When oxides and hydroxides of Ga(III) and In(III) are dissolved in alkalis, corresponding hydroxygallate and hydroxyindate ions are produced, e.g.

$$In(OH)_3 + 3OH^- = [In(OH)_6]^{3-}$$

Derivatives with an $\overset{+1}{M}_2[Ga_2O(OH)_6]$ and $\overset{+2}{M}_3[E(OH)_6]_2$ composition are usually precipitated from the solutions. When the E_2O_3 oxides are fused with basic oxides, oxycompounds of an $\overset{+1}{M}EO_2$ type are formed. Hydroxy- and oxygallates (indates) are similar to the corresponding aluminates in stability, solubility, and the character of their hydrolysis.

The *trihalides* of gallium and its analogues resemble $AlHal_3$ in many respects. The trifluorides EF_3, like AlF_3, have a coordination lattice (see Fig. 71) and are high-melting. The trichlorides ECl_3 have layer lattices, while EBr_3 and EI_3 (and also $GaCl_3$) have a molecular lattice consisting of E_2Hal_6 dimeric molecules, so that they are low-melting and volatile. Stability decreases in the EF_3—ECl_3—EBr_3—EI_3 series. Certain constants of the halides are given in the following table:

	InF_3	$InCl_3$	$InBr_3$	InI_3
$\Delta H^\circ_{f,298}$, kJ/mol	—1029	—537	—418	—247
$\Delta G^\circ_{f,298}$, kJ/mol	—962	—460	—372	—142
M. p., °C	1170	586	420	207

The trihalides dissolve in water, liberating heat. In the vapourous state and in organic solvents they exist in the form of E_2Hal_6 molecules, which are similar in structure to Al_2Hal_6 (see Fig. 190). The interaction of $EHal_3$ with basic halides yields complex halides, mainly of the $\overset{+1}{M}_3[EHal_6]$ and $\overset{+1}{M}[EHal_4]$ type:

$$3KHal + EHal_3 = K_3[EHal_6]$$

Fluorocomplexes are most characteristic of gallium(III), as of aluminium(III). Indium(III) and thallium(III), in contrast to Al(III) and Ga(III), form stable complexes with chlorine $[InCl_6]^{3-}$, $[TlCl_6]^{3-}$, bromine $[InBr_6]^{3-}$, and $[TlBr_6]^{3-}$, while Tl(III) also forms complexes with iodine.

The *hydrides* of gallium and indium (EH_3), like AlH_3, are polymers. Hydride gallates are also known, e.g. $Li[GaH_4]$, $Tl[GaH_4]_3$.

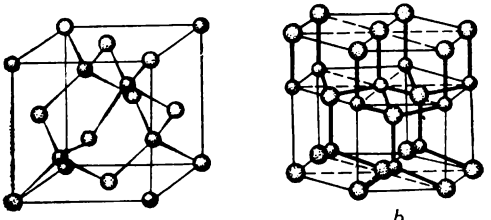
They are obtained in nonaqueous (ether) solutions:

$$GaCl_3 + 4LiH = Li[GaH_4] + 3LiCl$$

Indium(III) aluminium hydride can be regarded as a mixed hydride of aluminium and indium; it is formed by an exchange reaction in an ether medium:

$$InCl_3 + 3Li[AlH_4] = In[AlH_4]_3 + 3LiCl$$

The stability of compounds decreases in the BH_4^-—AlH_4^-—GaH_4^- series; $Li[GaH_4]$, for example, decomposes slowly at temperatures as low as 25 °C with the formation of LiH, Ga, and H_2. It is a mild



a *b*

Fig. 194. Crystal structure with tetrahedral bonds: (*a*) sphalerite; (*b*) wurtzite

reducing agent compared with $Li[AlH_4]$. The BH_4^- ion is quite stable in relation to water, while the salts of AlH_4^- and GaH_4^- react vigorously with water (often explosively):

$$EH_4^- + 4H_2O = 4H_2 + E(OH)_3 + OH^-$$

Compounds of Tl(III) are strong oxidants:

$$Tl^{3+} + 2e^- = Tl^+, \quad E^\circ_{298} = 1.25 \text{ V}$$

Like B and Al, gallium and indium react with Group V *p* elements to form compounds of the $A^{III}B^V$ type (where A^{III} is a Group III *p* element, and B^V a Group V *p* element). These compounds are isoelectronic with the corresponding simple substances of Group IV *p* elements. In compounds of the $A^{III}B^V$ type the atoms are in a state of sp^3 hybridisation, i.e. in tetrahedral coordination with one another. The main types of crystal structure with tetrahedral arrangement of the bonds are shown in Fig. 194.

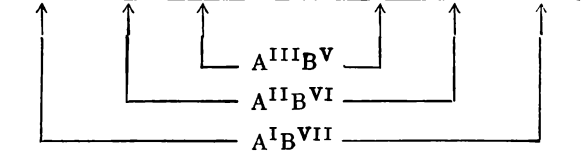
The names of the crystal structures shown in Fig. 194*a* and *b* originate from the corresponding forms of zinc sulphide ZnS, viz., *sphalerite* (cubic lattice) and *wurtzite* (hexagonal lattice).

Imitation of structure of the simple substances of Group IV *p* elements is also observed in certain binary compounds of the $A^{II}B^{VI}$ and A^IB^{VII} type (where A^{II} and A^I are Group II and I elements respectively, and B^{VI} and B^{VII} are Group VI and VII *p* elements).

In Table 43, which follows, the symbols of the elements yielding binary compounds with a tetrahedral arrangement of atoms, with

Table 43. Combinations of Elements Yielding Binary Compounds with Tetrahedral Coordination

I	II	III	IV	V	VI	VII
Li	**Be**	**B**	**C**	**N**	**O**	**F**
Na	**Mg**	**Al**	**Si**	**P**	**S**	Cl
Cu	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**
Au	Hg	Tl	Pb	Bi	Po	At



at least one element located equidistantly from Group IV elements are printed in bold type. The types of crystal lattices of the binary compounds formed by these elements are given in Table 44.

The similarity of the hybridisation of the valence orbitals of the atoms predetermines a far-reaching analogy between the simple substances of Group IV *p* elements and compounds formed by elements equidistant from Group IV. The internuclear distance in crystals AlP (0.235 nm), GaAs (0.243 nm), InSb (0.280 nm), for instance, is practically the same as in the isoelectronic crystals of Si (0.235 nm), Ge (0.245 nm), and α-Sn (0.280 nm). The same picture is observed with mean E_{AB} bond energies, which are similar in the isoelectronic simple substances, e.g. GaAs (150 kJ/mol) and Ge (163 kJ/mol), InSb (134 kJ/mol) and α-Sn (150 kJ/mol).

As in the C—Si—Ge—Sn—Pb series of simple substances, the strength of the covalent bond in the series of the isoelectronic compounds BN—AlP—GaAs—InSb—TlBi decreases, while the possibility of its delocalisation increases. Melting point and hardness accordingly diminish, the forbidden band becomes narrower

Table 44. Structure of Compounds of $A^{III}B^{V}$, $A^{II}B^{VI}$, and $A^{I}B^{VII}$ Type

	$A^{III}B^{V}$						$A^{II}B^{VI}$					$A^{I}B^{VII}$				
	N	P	As	Sb	Bi		O	S	Se	Te		F	Cl	Br	I
B	*s*	*s*	*s*	?	—	Be	*w*	*s*	*s*	*s*	Li	NaCl	NaCl	NaCl	NaCl
Al	*w*	*s*	*s*	*s*	—	Mg	NaCl	NaCl	NaCl	*w*	Na	NaCl	NaCl	NaCl	NaCl
Ga	*w*	*s*	*s*	*s*	—	Zn	*w*	*w*, *s*	*w*, *s*	*w*, *s*	Cu	*s*	*s*	*s*	*s*
In	*w*	*s*	*s*	*s*	CsCl	Cd	NaCl	*w*, *s*	*w*, *s*	*s*	Ag	NaCl	NaCl	NaCl	*w*, *s*
Tl	—	—	—	CsCl	CsCl*	Hg	—	*s*	*s*	*s*	Au	—	?	?	?

Symbols of structures: *s* – sphalerite type; *w* – wurtzite type; NaCl – rock salt type; and CsCl* – distorted CsCl type.

(Fig. 195), and the effective charge on the atom A^{III} decreases while the type of the crystal lattice alters in the transition from InSb to TlBi (as in the transition from α-Sn to Pb), for example:

	BN	AlP	GaAs	InSb	TlBi
Crystal lattice type	*s*	*s*	*s*	*s*	Face-centred cubic
d_{EX}, nm	0.158	0.235	0.243	0.280	—
E_{EX}, kJ/mol	—	210	150	134	—
M. p., °C	—	2000	1237	536	—
ΔE, eV	4.6	3.0	1.53	0.27	(metal)

The external form of the compounds is also evidence of this: BN looks like diamond, AlP is a yellow-grey mass, GaAs is a dark grey substance with a resinous lustre, InSb has the appearance of a light grey alloy with a metallic lustre, and TlBi is a metal alloy.

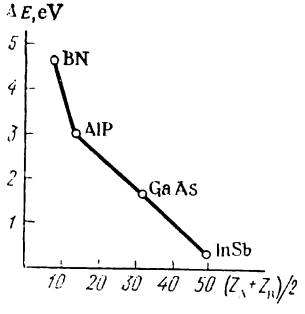


Fig. 195. Dependence of the width ΔE of the forbidden band in $A^{III}B^{V}$ compounds on the arithmetic mean of the atomic number

The properties of isoelectronic and isostructural compounds of the $A^{II}B^{VI}$ and $A^{I}B^{VII}$ type alter similarly in the subgroups, with increasing atomic number.

In the isostructural series of compounds of the $A^{III}B^{V}$—$A^{II}B^{VI}$— $A^{I}B^{VII}$ type, the role of the ionic bond increases as the difference in chemical nature of the elements becomes more marked and the forbidden band widens:

	Ge	GaAs	ZnSe	CuBr
ΔE, eV	0.78	1.53	2.6	2.94
Lattice type	diamond-like	*s*	*w*, *s*	*s*

A big group of compounds consisting of three, four, or more elements, of the $A^{I}B^{III}C_2^{IV}$ type ($CuInS_2$, $AgGaSe_2$, $CuAlS_2$), $A^{II}B^{IV}C_2^{V}$ type ($ZnSiP_2$, $CdGeAs_2$, $ZnGeAs_2$), and others, have a tetrahedral structure. A chalcopyrite type of structure ($CuFeS_2$, see Fig. 134) is characteristic of them.

Many diamond-like compounds are semiconductors, and therefore present great interest as materials for a.c. rectifiers, amplifiers, photoelectric cells, transducers, thermoelectric generators, etc. Many compete successfully with germanium and silicon as semiconductors.

Compounds of gallium(I), indium(I) and thallium(I). Many compounds are known for thallium(I); the derivatives of gallium(I) and indium(I) are unstable and are strong reducing agents.

The radius of the Tl^+ ion (0.144 nm) is close to those of the K^+ (0.133 nm), Rb^+ (0.148 nm), and Ag^+ (0.126 nm) ions, so that chem-

istry of thallium(I) resemble that of the alkali metals and silver. Tl(I) compounds are predominantly ionic and have high coordination numbers (six and eight); TlF, for example, has a structure of NaCl type, and TlCl, TlBr, and TlI of the CsCl type. Most Tl(I) compounds are soluble in water; TlF (like Ag^+) is readily soluble, but TlCl, TlBr, TlI, and Tl_2S (black) are insoluble.

Compounds of thallium(I) are basic in nature, either not hydrolysing or, if they do, forming an alkaline medium. The black *oxide* Tl_2O (m.p. 300 °C), for instance, is readily soluble in water

$$Tl_2O + H_2O = 2TlOH$$

The *hydroxide* TlOH (yellow) is a strong base but, unlike NaOH or RbOH, loses its water when heated (100 °C).

$$2TlOH\ (c) = Tl_2O\ (c) + H_2O\ (g), \qquad \Delta G^\circ_{298} = 5\ kJ$$

$$2RbOH\ (c) = Rb_2O\ (c) + H_2O\ (g), \qquad \Delta G^\circ_{298} = 206\ kJ$$

In this respect the chemistry of thallium resembles that of silver, whose hydroxide is unstable and decomposes during formation.

As with the alkali metals, complexation is not characteristic of thallium(I); it usually does not even form crystal hydrates. In complexation reactions, the Tl^+ ion usually passes into the outer sphere of complex compounds, for example,

$$3TlCl + TlCl_3 = Tl_3[TlCl_6]$$

$$\underset{\text{Basic}}{2TlNO_3} + \underset{\text{Acidic}}{Tl(NO_3)_2} = Tl_2[Tl(NO_3)_5]$$

Like silver(I) compounds, the thallium(I) compounds are photosensitive and decompose on exposure to light. Thallium(I) derivatives can be converted into thallium(III) compounds by the action of strong oxidants.

Compounds of gallium, indium, and thallium are poisonous!

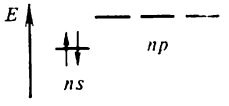
CHAPTER 8

Group II *s* Elements

The Group II *s* elements are the *typical* elements beryllium Be and magnesium Mg and the elements of the *calcium subgroup*, viz., calcium Ca, strontium Sr, barium Ba, and radium Ra. Important characteristics of these elements are as follows:

	$_4$Be	$_{12}$Mg	$_{20}$Ca	$_{38}$Sr	$_{56}$Ba	$_{88}$Ra
Atomic mass	9.01	24.31	40.08	37.62	137.34	[226]
Valence electrons	(2)$2s^2$	(8)$3s^2$	(8)$4s^2$	(8)$5s^2$	(8)$6s^2$	(8)$7s^2$
Metal atomic radius, nm	0.113	0.160	0.197	0.215	0.221	0.235
Ion E^{2+} radius, nm	0.034	0.074	0.104	0.120	0.138	0.144
$E^0 \rightarrow E^+$ ionisation energy, eV	9.32	7.65	6.11	5.69	5.21	5.28
$E^+ \rightarrow E^{2+}$ ionisation energy, eV	18.21	15.04	11.87	11.0	10.0	10.1
Abundance, mole per cent	1.2×10^{-3}	2.0	2.0	1×10^{-2}	5.7×10^{-3}	1×10^{-10}

In accordance with the structure of the valence electron layer



Group II *s* elements have a +2 oxidation state.

The ionisation energy of the atoms of these elements decreases, as in the other main subgroups, the atomic and ionic radii increase, and their metallic character strengthens with increasing atomic number.

8.1. Beryllium

Beryllium ($1s^22s^2$) is more metallic than boron ($1s^22s^22p^1$), and its nonmetallic properties are less pronounced (in accordance with the increased radius of the atom and lower number of valence electrons). Beryllium has higher ionisation energies ($I_1 = 9.32$ eV, $I_2 = 18.21$ eV) than the other Group II *s* elements. At the same time, it is very similar to aluminium (diagonal likeness in the periodic system) and is a typical amphoteric element; in normal conditions it does not form simple ions, both cation and anion complexes being characteristic of it. Its oxidation state in all its stable compounds is +2. The most characteristic coordination number of beryllium(II) is four (sp^3 hybridisation of the valence orbitals).

Berillium is found in the Earth's crust as the isotope ^{9}Be (0.001 mole per cent). Its most important minerals are *beryl* $Be_3Al_2(SiO_3)_6$ and *phenacite* Be_2SiO_4. Certain transparent varieties, coloured by admixtures (green *emeralds*, bluish *aquamarines*, etc.) are gem stones. They are now made artificially.

The simple substance. Beryllium is a light grey metal (m.p. 1284°C, b.p. 2970 °C) with a dense hexagonal crystal lattice. It is quite hard and brittle. Like aluminium, it becomes coated with an oxide film that dulls its surface and reduces its chemical activity. When heated, it burns in oxygen and air, and reacts readily with sulphur and

nitrogen; with the halogens it reacts at normal temperatures or with slight heating. All these reactions are accompanied with the liberation of considerable heat because of the great stability of the lattices of the reaction products BeO, BeS, Be_3N_2, etc. In ordinary conditions beryllium does not react with hydrogen.

The protective oxide film prevents an interaction of beryllium and water ($E^\circ_{298} = -1.85$ V), but like aluminium, it reacts with acids and alkalis with liberation of hydrogen to form cation and anion complexes:

$$Be + 2OH_3^+ + 2H_2O = [Be(OH_2)_4]^{2+} + H_2$$
$$Be + 2H_2O + 2OH^- = [Be(OH)_4]^{2-} + H_2$$

Beryllium (like aluminium) is passivated in concentrated cold nitric and sulphuric acid.

With metals, beryllium forms intermetallic compounds. The *beryllides* of certain *d* elements with an MBe_{12} composition (M = Ti, Nb, Ta, Mo), or MBe_{11} (M = Nb, Ta) and other compositions have high melting points and are stable at temperatures between 1200 °C and 1600 °C.

Beryllium is of major importance as an alloying additive, giving alloys heightened resistance to corrosion and increased strength and hardness. *Beryllium bronzes* (Cu-Be alloys containing up to 2.5 per cent of beryllium) are its most valuable alloys. Beryllium alloys are employed in the aircraft industry, electrical engineering, etc.

Beryllium is used as a moderator and reflector of neutrons in atomic reactors. Its mixtures with radium preparations are used as sources of neutrons, which are formed by the action of alpha particles on ^9Be:

$$^9_4Be + ^4_2He = ^{12}_6C + ^1_0n$$

Beryllium is obtained by thermal reduction of its halides by magnesium.

Compounds of beryllium(II). In normal conditions most inorganic compounds of beryllium(II) are white crystalline polymers. Its coordination number is four, irrespective of the type of the compounds' crystal lattice. In acidic aquo solutions the Be^{2+} ions are present as stable aquo complexes $[Be(OH_2)_4]^{2+}$ and in strongly alkaline solutions as $[Be(OH)_4]^{2-}$ ions.

The *oxide* BeO has a wurtzite type structure (see Fig. 194), and high lattice energy and Gibbs' energy ($\Delta G^\circ_f = -582$ kJ/mol) of formation. It is refractory (m.p. 2530 °C) and conducts heat. After calcining (400 °C) BeO becomes highly stable chemically. It is used as a chemically stable, refractory material in the manufacture of crucibles and special ceramic articles, and as a moderator and reflector of neutrons in nuclear reactors. BeO is a constituent of certain glass-forming mixtures.

Being amphoteric, BeO reacts on fusing with basic and acidic oxides

$$\underset{\text{Basic}}{BeO + SiO_2 = BeSiO_3}, \qquad \underset{\text{Acidic}}{BeO + Na_2O = Na_2BeO_2}$$

When heated, it reacts with acids and alkalis

$$\underset{\text{Basic}}{BeO + 2OH_3^+ + H_2O = [Be(OH_2)_4]^{2+}} \quad \text{and} \quad \underset{\text{Acidic}}{BeO + H_2O + 2OH^- = [Be(OH)_4]^{2-}}$$

The *hydroxide* $Be(OH)_2$ is a water-insoluble polymer. It is obtained by the following summary equation, which also illustrates its attitude to acids and alkalis:

$$[Be(OH_2)_4]^{2+} \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} Be(OH)_2 \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} [Be(OH)_4]^{2-}$$

As will be seen from the equation, aquo complexes of beryllium(II) are stable in acidic media (excess OH_3^+ ions), while hydroxyberyllate(II) complexes are stable in alkaline media (excess OH^- ions). When crystallised from acidic aqueous solutions, aquo complexes are converted into crystal hydrates with four molecules of water: $BeSO_4 \cdot 4H_2O$, $BeCl_2 \cdot 4H_2O$, $Be(NO_3)_2 \cdot 4H_2O$, etc. The varying number of water molecules in the crystal hydrates indicates that derivatives of polynuclear complexes are formed.

Because of the comparatively high polarising action of the Be^{2+} ion, its salts are appreciably hydrolysed:

$$[Be(OH_2)_4]^{2+} + H_2O \rightleftharpoons [Be(OH)(OH_2)_3]^+ + OH_3^+$$

The mechanism of hydrolysis can differ substantially depending on the concentration of the solution and the type of anions present in it. The hydroxyaquo complex $[Be(OH)(OH_2)_3]^+$, for example, which is formed during hydrolysis, is then polymerised into a polynuclear complex $[Be_3(OH)_3(OH_2)_6]^{3+}$ that probably has the following structure:

$$3[Be(OH)(OH_2)_3]^+ \rightleftharpoons \left[\begin{array}{c} H_2O \quad OH_2 \\ H \\ H_2O \diagdown \quad O-Be \quad \diagup OH \\ Be \\ H_2O \diagup \quad O-Be \quad \diagdown OH \\ H \\ H_2O \quad OH_2 \end{array} \right]^{3+} + 3H_2O$$

or $$3Be^{2+} + 3HOH \rightleftharpoons [Be_3(OH)_3]^{3+} + 3H^+; \quad pK = -8.66.$$

When the OH_3^+ ion is bound (e.g. with CO_3^{2-} or SH^- ions) polymerisation may continue to the formation of a polymeric hydroxide:

$$BeS + 2H_2O = Be(OH)_2 + H_2S$$

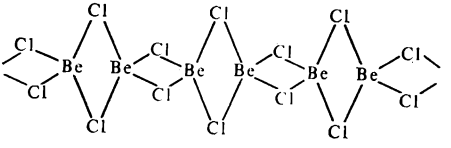
Hydroxyberyllates can only exist in aqueous solutions in the presence of a big excess of alkali, otherwise they are completely hydrolysed. Only beryllates of Group I *s* elements are soluble.

Beryllium *sulphide* BeS is a crystalline solid with a sphalerite type structure (see Fig. 194*a*). It is formed by the interaction of the simple substances (at 1350 °C) or by the reaction of the metal with H_2S. BeS is completely hydrolysed in hot water. Its amphoteric nature is displayed during fusion with basic and acidic sulphides:

$$Na_2S + BeS = Na_2BeS_2, \qquad BeS + SiS_2 = BeSiS_3$$

Sulphide beryllates(II) are decomposed by water.

Beryllium fluoride and beryllium chloride are the most important *halides* of beryllium. BeF_2 exists in several forms that are similar in structure to the corresponding varieties of silicon dioxide SiO_2 (cf. Fig. 60 and 70*c*). Like silica, BeF_2 is easily vitrified. Glass-like BeF_2 is obtained by the thermal decomposition of $(NH_4)_2BeF_4$. The other Be(II) halides are also polymorphous. One $BeCl_2$ form has a fibrous structure



Because of their coordination structure, the melting points of the corresponding forms of BeF_2 are higher (about 800 °C) than those of the other beryllium(II) halides (about 450 °C). The $BeCl_2$, $BeBr_2$, BeI_2 halides are hygroscopic and deliquescent in air, and dissolve in water with liberation of heat. They are also soluble in organic solvents.

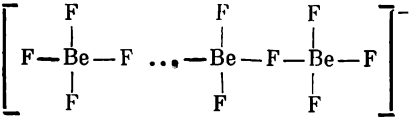
The amphoteric properties of $BeHal_2$ are more pronounced in the fluoride. When BeF_2, for example, is heated with basic fluorides, fluoberyllates (Fig. 196) are formed: e.g.

$$2KF + BeF_2 = K_2[BeF_4]$$

BeF_2 reacts with acidic fluorides to form salts of beryllium:

$$BeF_2 + SiF_4 = Be[SiF_6]$$

The tetrafluoberyllates resemble the similar tetraoxysulphates in crystal structure (Fig. 197) and solubility, which is due to an identical tetrahedral structure and the similar size of the BeF_4^{2-} and SO_4^{2-} ions. In addition to the BeF_4^{2-} ion, polymeric fluoberyllate ions of the following type are also possible:



The sodium fluoberyllate $NaBeF_3$ is built from the similar chain anions.

The structural likeness of BeF_2 and SiO_2 extends to their derivatives. Polymeric fluoberyllates are similar in structure to oxysilicates, $NaBeF_3$ for example, has the same structure as $CaSiO_3$; Na_2BeF_4 is

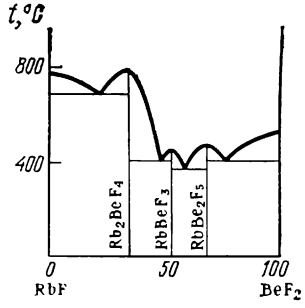


Fig. 196. Phase diagram of a $RbF—BeF_2$ system

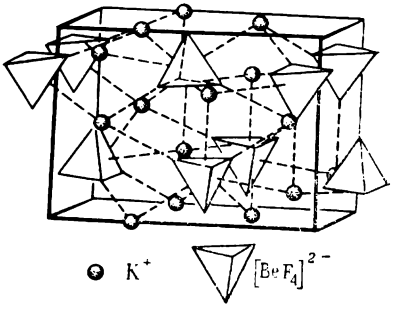


Fig. 197. Structure of K_2BeF_4

similar to Ca_2SiO_4, $NaLiBeF_4$ to $CaMgSiO_4$, Li_2BeF_4 to Zn_2SiO_4, and so on. The phase diagrams of the corresponding systems are also similar. Fluoberyllate polymers can exist in a vitreous state.

Other halogen beryllates are not characteristic.

The tendency of the amphoteric element beryllium to form cation and anion complexes is seen during the melting of its compounds. Molten $BeCl_2$, for instance, consists of $BeCl^+$ and $BeCl_3^-$ ions:

$$\underset{\text{Basic}}{BeCl_2} + \underset{\text{Acidic}}{BeCl_2} \rightleftarrows BeCl^+ + BeCl_3^-$$

Other molten amphoteric elements behave in a similar way:

$$2AlCl_3 \rightleftarrows AlCl_2^+ + AlCl_4^-, \quad 2TaCl_5 \rightleftarrows TaCl_4^+ + TaCl_6^-$$

In this case, too, amphoteric elements do not form simple ions, but complex ones. The similar compounds of metallic elements disintegrate in these conditions into poorly solvated simple ions:

$$CaCl_2 \rightleftarrows Ca^{2+} + 2Cl^-$$

Because of this the molten compounds of metallic elements have a high electrical conductivity and those of amphoteric elements a low one.

Beryllium *nitride* Be_3N_2 is a crystalline substance obtained by heating beryllium in a nitrogen atmosphere (above 1000 °C). It is colourless, very hard, refractory (m.p. 2200 °C), but is decomposed

by water when heated:

$$Be_3N_2 + 6H_2O = 3Be(OH)_2 + 2H_3N$$

It is quite actively destroyed by acids.

The amphoteric properties of Be_3N_2 are demonstrated by the existence of mixed nitrides, e.g. $BeSiN_2$ and LiBeN, which can be regarded as beryllium nitride silicate(IV) and lithium nitride beryllate(II) respectively.

Beryllium *hydride* BeH_2 is a solid polymer similar in properties to AlH_3. It decomposes in water with liberation of hydrogen and is a strong reductant. It cannot be formed from the simple substances ($\Delta G_f^\circ = 115.7$ kJ/mol), but only by the reaction of $BeCl_2$ and LiH in an ether solution:

$$BeCl_2 + 2LiH = BeH_2 + 2LiCl$$

Salts of beryllium and oxyacids are precipitated from solution as crystal hydrates that differ substantially from the anhydrous derivatives in structure and properties. Most beryllium salts are soluble in water, but $BeCO_3$, $Be_3(PO_4)_2$, and certain others are insoluble. Double salts, beryllates with complex ligands, are quite characteristic: e.g.

$$Na_2SO_4 + BeSO_4 = Na_2[Be(SO_4)_2]$$
$$(NH_4)_2CO_3 + BeCO_3 = (NH_4)_2[Be(CO_3)_2]$$

Through the second reaction water-insoluble $BeCO_3$ dissolves in saturated solutions of carbonates of Group I *s* elements or of ammonia. In dilute solutions these beryllates decompose.

Beryllium compounds are poisonous!

8.2. Magnesium

Magnesium differs markedly from beryllium in the size of its atom and ion (the radii of the ions Be^{2+} and Mg^{2+} being 0.034 and 0.078 nm respectively). Magnesium differs from aluminium, its neighbour in the period, by its smaller number of valence electrons and a relatively larger atom. Its metallic character is thus more pronounced than that of beryllium and aluminium. The formation of covalent bonds is less characteristic of magnesium than of beryllium and aluminium, and the formation of ionic bonds more characteristic. In this respect it is closer to the typical metals (elements of the calcium subgroup).

Magnesium is one of the most abundant elements (2.0 mole per cent). Three stable isotopes occur in nature, viz., ^{24}Mg (78.6 per cent), ^{25}Mg (10.11 per cent), and ^{26}Mg (11.29 per cent). Artificial isotopes have also been obtained. Magnesium occurs in silicate minerals (mostly *olivine*, Mg_2SiO_4), and the carbonate minerals *dolomite*

$CaMg(CO_3)_2$ and *magnesite* $MgCO_3$; *carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$ is of great technical importance. Sea water contains much magnesium (up to 0.38 per cent $MgCl_2$) and in the water of certain salt lakes (up to 30 per cent $MgCl_2$).

The simple substance. Magnesium is a white metal (density 1.74 g/cm³, m.p. 651 °C, b.p. 1107 °C), softer and more plastic than beryllium. It is dulled by oxidation by atmospheric oxygen.

Magnesium is an active metal that reacts readily with halogens, burns in air when heated, and is oxidised by sulphur and nitrogen. With other metals it forms eutectic mixtures, solid solutions, and intermetallic compounds, which are part of its alloys. The most important magnesium alloy is *electron* (Al 3-10 per cent, Zn 0.2-3 per cent, the rest Mg). Because of its strength and light weight (1.8 g/cm³) it is used in aerospace technology.

Magnesium comes before hydrogen in the electromotive series ($E^\circ_{298} = -2.36$ V). It reacts very slowly with cold water because the resulting hydroxide $Mg(OH)_2$ is poorly soluble; the reaction, however, is accelerated by heat (the $Mg(OH)_2$ being dissolved). It is dissolved energetically by acids (except by HF and H_3PO_4, which form barely soluble compounds with magnesium). It does not react at all with alkalis.

The bulk of commercial magnesium is obtained by electrolysis of molten carnallite or $MgCl_2$, to which NaCl or other chlorides are added to lower the melting point (to 720 °C —750 °C). The magnesium is recovered at the cathode, while the chlorine evolved at the anode is used to make $MgCl_2$. Magnesium is also obtained by metallothermic and carbothermic techniques. With the first method, calcined dolomite $CaO \cdot MgO$ is reduced by ferrosilicon or aluminosilicon at 1200 °C to 1300 °C in electric furnaces:

$$2(CaO \cdot MgO) + Si = Ca_2SiO_4 + 2Mg$$

In the second method magnesium is obtained by reducing it by carbon in electrical furnaces at 2100 °C. Pure magnesium (99.999 per cent Mg) is obtained by repeated vacuum sublimation of commercial magnesium.

Magnesium is mainly used to make light alloys and to obtain Ti, Zr, V, U, and other metals (by metallothermy). Mixtures of magnesium powder and oxidising agents are used in flares and star shells, incendiary bombs, flash photography, and various pyrotechnical devices.

Compounds of magnesium(II). Magnesium has a +2 oxidation state and the coordination number of six in all its stable compounds. A +2 oxidation state is also displayed in its intermetallic compounds, e.g. Mg_2Al_3, Mg_3Sb_2, Mg_2Pb. Its binary compounds may vary, depending on the nature of the more electronegative element, from predominantly metallic to predominantly ionic; in the series of

compounds with third period *p* elements, for instance, the proportion of the metallic bond gradually decreases and that of the ionic bond increases:

	Mg_2Si	Mg_3P_2	MgS	$MgCl_2$
$\Delta H^\circ_{f,298}$, kJ/mol	—26	—107	—177	—641
Coordination number				
of Mg	4	4	6	6
of E	8	6	6	3

Mg_3Al_2, for example, is a typical metallic compound while $MgCl_2$ is predominantly ionic. This is also indicated by the rising enthalpies of formation of compounds in this series, and the character of the changes in the coordination number of their crystals.

Magnesium(II) compounds are predominantly basic in nature. Some of them, e.g. $MgCl_2$, $MgSO_4$, and $Mg(NO_3)_2$, are not hydrolysed in normal conditions; others produce weakly alkaline media.

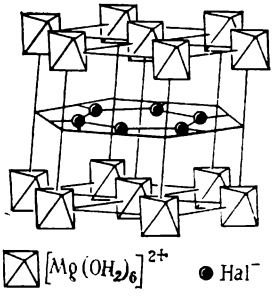


Fig. 198. Structure of bischofite $MgCl_2 \cdot 6H_2O$

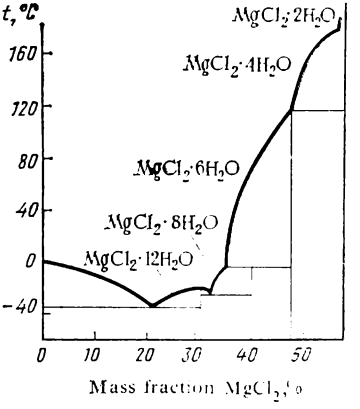


Fig. 199. Phase diagram of an H_2O—$MgCl_2$ system

Most magnesium(II) compounds are soluble in water, but the salts of weak acids ($Mg_3(PO_4)_2$, $MgCO_3$, MgF_2) are poorly soluble. In aqueous solutions the ion Mg^{2+} has the form of colourless hexaaquo complexes $[Mg(OH_2)_6]^{2+}$, which are part of certain of its crystal hydrates, viz., $MgCl_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Mg(ClO_4)_2 \cdot 6H_2O$, $MgSiF_6 \cdot 6H_2O$, and others. The structure of magnesium dichloride hexahydrate $MgCl_2 \cdot 6H_2O$ (*bischofite*) is shown in Fig. 198. There are also crystal hydrates containing from one to twelve molecules of water (Fig. 199).

The anhydrous salts of Mg(II) are quite hygroscopic, especially $Mg(ClO_4)_2$, *anhydrone*, which avidly takes up water (to 60 per cent of

its own mass) and is widely used for drying gases (H_2, CO_2, O_2, H_2S, etc.).

Anion complexes are not characteristic of Mg(II), but there are many double salts, like the mixed carbonate $CaCO_3 \cdot MgCO_3$ (*dolomite*), the double nitride $Li_3N \cdot Mg_3N_2$ (LiMgN), etc. Crystal hydrates $KCl \cdot MgCl_2 \cdot 6H_2O$ (*carnallite*), $M_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ (*schoenites*), etc., are also quite characteristic.

Magnesium *oxide* MgO (*light-burnt magnesia*) is a high-melting (m.p. 2800 °C) substance obtained industrially by thermal decomposition of the magnesium carbonate

$$MgCO_3 \rightleftharpoons MgO + CO_2$$

Its fine crystalline powder is a chemically active basic compound, that reacts with water, absorbs CO_2, and readily dissolves in acids. When strongly heated it becomes very hard and unreactive.

Magnesia is used in the production of magnesium metal, as a filler in the manufacture of rubber, in the refining of oil products, in the production of refractories and building materials.

Magnesium *hydroxide* $Mg(OH)_2$ is a crystalline solid with a layer structure (see Fig. 232*a*). It is only slightly soluble in water and is a base of medium strength ($K_{b_2} = 2.5 \times 10^{-3}$). In particular, it displaces ammonia from saturated solutions of NH_4^+ compounds:

$$2NH_4Cl + Mg(OH)_2 = MgCl_2 + 2H_3N + 2H_2O$$

In addition to the oxide, $MgCl_2$, magnesium dichloride, is also widely used. Its crystals are formed by octahedral $MgCl_6$ unit cells united in layers (see Fig. 232*b*). The dichloride is prepared by chlorinating MgO in the presence of coal

$$MgO + Cl_2 + C = MgCl_2 + CO$$

or by dehydrating $MgCl_2 \cdot 6H_2O$ recovered from sea water. It is mainly used in the production of magnesium metal and in making *Sorel's* (*magnesian*) *cement*. Magnesium oxychloride cement is made by mixing calcined MgO with a 30 per cent aqueous solution of $MgCl_2$. Polymer chains are formed in this reaction to yield a quick setting hard white mass that is stable to acids and alkalis.

Magnesium does not react directly with hydrogen, but the hydride MgH_2 can be obtained indirectly. The ionic bond is more pronounced in MgH_2 than in the predominantly covalent hydrides BeH_2 and AlH_3. Magnesium hydride is a nonvolatile solid, thermally more stable than the hydrides of beryllium and aluminium. It is decomposed by water. A hydroborate $Mg[BH_4]_2$ and hydroaluminate $Mg[AlH_4]_2$ are also known.

8.3. Calcium Subgroup

Calcium Ca, strontium Sr, barium Ba, and radium Ra have bigger atomic radii and lower ionisation potentials than the typical elements beryllium and magnesium (see p 472). They therefore easily give up their valence electrons in chemical interactions and form simple ions E^{2+}. Since E^{2+} ions have an s^2p^6 electron configuration and are comparatively large (i.e. weakly polarised), complex ions of the calcium subgroup elements with inorganic ligands are unstable.

Calcium is found in the crust as a mixture of six stable isotopes, strontium of four, and barium of seven. The most abundant are ^{40}Ca (96.97 per cent), ^{88}Sr (82.56 per cent) and ^{138}Ba (71.66 per cent). Radium has no stable isotopes.

Calcium is one of the most abundant elements (2.0 mole per cent). Most of it is contained in igneous rocks (granite, gneiss, etc.) in the form of silicates and aluminosilicates. The commonest of its other rocks are *limestone* and *chalk*, which consist mainly of the mineral *calcite* $CaCO_3$. The crystallised form of a mixture of calcite and dolomite, known as *marble*, is less common. *Anhydrite* $CaSO_4$ and *gypsum* $CaSO_4 \cdot 2H_2O$ are widely distributed. *Fluorite* (or fluorspar) CaF_2, *apatite* $Ca_5(PO_4)_3$ (F, Cl, OH), and other calcium minerals are very important in industry. Most natural waters contain calcium compounds as products of the weathering of minerals; they are a main cause of the hardness of water.

The most important strontium and barium minerals are *strontianite* $SrCO_3$, *witherite* $BaCO_3$, *celestine* $SrSO_4$, and *baryte* (or *heavy spar*) $BaSO_4$. Radium occurs in uranium ores.

The simple substances. Calcium and its analogues are silvery-white metals, but soon become coated in air with a yellowish film, the product of their reaction with the constituents of air. Calcium is quite hard, strontium and barium are softer, while barium resembles lead in this respect. The main constants of these metals (compared with Be and Mg) are as follows:

	Be	Mg	Ca	Sr	Ba	Ra
Density, g/cm³	1.85	1.74	1.54	2.63	3.76	about 6
Crystal lattice	hexagonal	hexagonal	fcc hex.	fcc hex.	bcc	
M. p., °C	1283	650	850	770	710	960
B. p., °C	2970	1117	1490	1370	1640	1530
ΔS°_{298}, J/K·mol	9.5	32.7	41.6	53.1	67	71
Electrical conductivity	5	21	21	4	—	—
$\Delta H^\circ_{\text{subl, 298}}$, kJ/mol	320.55	150.2	191.0	164.0	195.0	—
E°_{298} $E^{2+}+2e^- = E$, V	—1.85	—2.36	—2.87	—2.89	—2.90	—

In normal conditions calcium, strontium, and barium react vigorously with active nonmetals. The alkaline earth metals react with less active nonmetals, like nitrogen, hydrogen, carbon, silicon, etc., when more or less strongly heated, the reactions being accompanied with the liberation of much heat. Activity increases through the series Ca—Sr—Ba. When heated, the alkaline earth metals react with the other metals to form alloys containing various intermetallic compounds.

Calcium and its analogues are much higher than hydrogen in the electromotive series. They dissolve even in cold water, since the resulting hydroxides are more or less soluble. The activity of the reaction with water increases noticeably in the Ca—Sr—Ba series.

Calcium and strontium are obtained by electrolysis of their molten chlorides. Barium of high purity is obtained from BaO by aluminothermy.

Because of their high chemical activity, the alkaline earth metals are stored in kerosene in sealed vessels (calcium usually in tightly sealed cans).

Compounds of calcium(II), strontium(II), and barium(II). Inorganic compounds of calcium and its analogues are crystalline solids, mostly melting at high temperatures.

The *oxides* are prepared in the laboratory by thermal decomposition of the corresponding carbonates or nitrates:

$$CaCO_3 \rightleftharpoons CaO + CO_2, \qquad 2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2$$

In industry they are obtained by thermal decomposition of natural carbonates. The oxides react vigorously with water to form more or less soluble bases $E(OH)_2$, with liberation of much heat

$$EO\ (c) + H_2O\ (l) = E(OH)_2\ (c), \qquad \Delta H^\circ_{hydr\ EO}$$

The enthalpy of hydration ΔH_{hydr} increases in the series CaO—SrO—BaO.

The *hydroxides* $E(OH)_2$ are strong bases, inferior only to those of Group I *s* elements. Data on the oxides and hydroxides of these elements (compared with Be and Mg) are given in the following table:

	Be	Mg	Ca	Sr	Ba
Ion E^{2+} radius, nm	0.034	0.074	0.104	0.120	0.133
M. p. of EO, °C	2520	2800	2585	2430	1923
$\Delta H^\circ_{hydr.\ EO}$, kJ/mol	—23	—37	—65	—83	—106
Solubility of $E(OH)_2$ at 20°C mol/litre	8×10^{-6}	5×10^{-4}	2×10^{-2}	7×10^{-2}	2×10^{-1}
K_{b_2}	—	2.5×10^{-3}	4.0×10^{-2}	1.5×10^{-1}	2.3×10^{-1}

The basic character of hydroxides increases in the series $Be(OH)_2$ — $Mg(OH)_2$ — $Ca(OH)_2$—$Sr(OH)_2$—$Ba(OH)_2$; so, too, do their solubility and thermal stability.

A solution of $Ba(OH)_2$ (*baryta water*) is an important reagent for identifying CO_2. The hydroxide $Ca(OH)_2$ (*milk of lime, slaked lime*) is used as a cheap soluble base.

The increase in basic properties of the oxides in the transition from BeO to BaO is seen from the change in the ΔG of their interaction with corresponding acidic oxides. Thus, ΔG°_{298} of the reactions

$$EO\ (c) + CO_2\ (g) = ECO_3\ (c)$$

$$EO\ (c) + SO_3\ (s) = ESO_4\ (c)$$

$$EO\ (c) + SiO_2\ (s) = ESiO_3\ (c)$$

increases with the atomic number of E (Fig. 200). The strengthening of basic properties in the $Ca(OH)_2$—$Sr(OH)_2$—$Ba(OH)_2$ series can be demonstrated in a similar way by considering the ΔG°_{298} of the formation of ECO_3

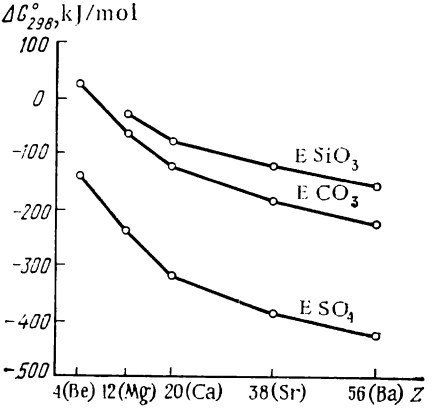


Fig. 200. Dependence of the ΔG of the formation of $ESiO_3$, ECO_3, and ESO_4 from oxides on the atomic number of E

$$E(OH)_2\ (c) + CO_2\ (g) = ECO_3\ (c) + H_2O\ (l)$$

	$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
ΔG°_{298}, kJ/mol	30	—38	—75	—110	—112

The increasing stability of the salts with anions of similar complexity is further evidence of the increase in basic properties of similar compounds in the Ca(II)—Sr(II)—Ba(II) series. The thermal stability of carbonates of the alkaline earth metals has already been discussed (p 263). Here is another example

$$EBeF_4\ (c) = EF_2\ (c) + BeF_2\ (c)$$

As the basic character increases in the CaF_2—SrF_2—BaF_2 series, stability markedly increases in the $CaBeF_4$—$SrBeF_4$—$BaBeF_4$ series: barium fluoberyllate melts without decomposition at 1080 °C, while calcium fluoberyllate decomposes into CaF_2 and BeF_2 when heated to 890 °C.

Only ECl_2, EBr_2, EI_2, and $E(NO_3)_2$ are readily soluble in water; other salts and salt-like compounds (ES, $E(OH)_2$, $E(SH)_2$), are more or less soluble and so are most of the acidic salts ($E(HSO_4)_2$, $E(HCO_3)_2$, etc.).

The salts and salt-like compounds of calcium and its analogues either do not hydrolyse ($EHal_2$, $E(NO_3)_2$, $ESiF_6$ etc.), or produce an alkaline medium:

$$EH_2 + 2H_2O = E(OH)_2 + 2H_2, \qquad E_3N_2 + 6H_2O = 3E(OH)_2 + 2H_3N$$

Certain crystal hydrates, e.g. $CaCl_2 \cdot 6H_2O$ and $[Ca(OH_2)_6]Cl_2$, can be considered as derivatives of cation complexes of Ca(II) and its analogues. The tendency to form crystal hydrates explains their hygroscopicity; $CaCl_2$, in particular, is used as a dehydrating agent because of its high hygroscopic properties.

The anhydrous chlorides, bromides, and iodides also tend to unite with H_3N to form ammoniates $EHal \cdot 8H_3N$, which become slightly less stable in the Ca—Sr—Ba series. A pressure of 6×10^4 Pa of ammonia is reached in $[Ca(NH_3)_8]I_2$, for instance, at 96 °C, in $[Sr(NH_3)_8]I_2$ at 62 °C and in $[Ba(NH_3)_8]I_2$ at 20 °C. The ammoniates are easily decomposed by water.

With basic compounds, salts of Ca(II), Sr(II), and Ba(II) form either solid solutions ($KMnO_4$—$BaSO_4$ and KBF_4—$BaSO_4$) or eutectic mixtures (NaCl—$BaCl_2$ and $CaCl_2$—$BaCl_2$).

The high activity of calcium and its analogues is also seen in their tendency to form numerous peroxide compounds, e.g. *peroxides* EO_2, *superoxides* $E(O_2)_2$, *persulphides* ES_n (n = 2-5), and *percarbides* EC_2, whose stability increases in the series Ca(II)—Sr(II)—Ba(II).

The elements of the calcium subgroup also form anion complexes, e.g. $Na_4[CaCl_4]$, $Na_4[BaCl_4]$, and $Na_4[Ca(OH)_6]$.

Cementing materials. Natural compounds of calcium are widely used in production of *binding* agents, powdered substances that form a plastic mass when mixed with water and set into a strong solid. Binding agents are used in mortars to bind brick and stone and separate structural elements, in the preparation of concrete, construction units, and large structures. They include *cements*, *gypsum materials*, *limes*, etc.

Chemically cements are mainly silicates and aluminates of calcium, i.e. contain Si and Al, elements especially liable to form heterochain polymers (based on Si—O—Si and Al—O—Al bonds). Various types of cement are distinguished according to silicate and aluminate content, namely, *silicate cement* (*Portland cement*) and *aluminate* (*aluminous*) *cement*.

Silicate cements are synthesised by calcining a finely ground mixture of limestone and clays rich in SiO_2 at 1400 °C to 1600 °C until the Si—O—Si and Al—O—Al bonds are partly broken to form silicates and aluminates relatively simple in structure, with liberation of CO_2. When the finely ground clinker is mixed with water, a pasty mass is obtained that gradually sets. The hardening (setting) of cement is due to complicated processes of the hydration and polycondensation of the constituents of the clinker, resulting in the formation of high-molecular calcium silicates and aluminates.

The main gypsum material, *plaster of Paris* or *alabaster*, a hydrate of $2CaSO_4 \cdot H_2O$ composition, is produced by calcining gypsum at

150 °C to 180 °C. When powdered $2CaSO_4 \cdot H_2O$ is mixed into a paste with water, hydration occurs and the mass hardens, owing to crystallisation:

$$2[CaSO_4 \cdot 0.5H_2O] + 3H_2O = 2[CaSO_4 \cdot 2H_2O]$$

This property of gypsum accounts for its wide use in the making of wall boards and panels, casting moulds and replicas, in plasters, etc.

A mixture of slaked lime and sand and water is also used as a *mortar*. It hardens through the transition of $Ca(OH)_2$ into crystalline $CaCO_3$, through absorption of CO_2 from the air:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Calcium silicates are formed at the same time (because of the presence of SiO_2).

Hardness of water. As already said, the presence of calcium and magnesium salts in natural water makes it hard. Temporary and permanent hardness of water are distinguished: *temporary hardness* is due to the presence of hydrocarbonates, and *permanent hardness* to sulphates and chlorides of Ca(II) and Mg(II).

Water can be softened by physical and chemical means. Temporary hardness is removed by boiling, the hydrocarbonates being transformed into insoluble carbonates and precipitated:

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O$$

Chemical softening is based on adding reagents to water that enrich it with CO_3^{2-} and OH^- anions, so that barely soluble $CaCO_3$ and $Mg(OH)_2$ are produced. Slaked lime and soda are used for the purpose:

$$CaSO_4 \text{ (sol)} + Na_2CO_3 \text{ (sol)} = CaCO_3 \text{ (s)} + Na_2SO_4 \text{ (sol)}$$
$$Ca(HCO_3) \text{ (sol)} + Ca(OH)_2 \text{ (sol)} = 2CaCO_3 \text{ (s)} + 2H_2O \text{ (l)}$$
$$MgSO_4 \text{ (sol)} + Ca(OH)_2 \text{ (sol)} = Mg(OH)_2 \text{ (s)} + CaSO_4 \text{ (sol)}$$

Sodium phosphates, borax, potash, etc., can also be used to remove Ca^{2+} and Mg^{2+} ions.

An *ion-exchange* method is now widely employed in industry to soften water. The capacity of certain high-molecular natural and synthetic materials (ion exchangers, or ionites) to exchange their radicals for ions in solution is utilised in the method.

Cation and *anion exchangers* are distinguished according to the type of exchange. Cation exchangers are aluminosilicates, like zeolites, e.g. $Na_2[Al_2Si_2O_8] \cdot nH_2O$, and artificially synthesised hydrated *permutites*, several silicates, and other materials. The exchange of ions between the aluminosilicates and hard water can be expressed

schematically as follows:

$$Na_2R + Ca(HCO_3)_2 \rightleftharpoons CaR + 2NaHCO_3$$

$$Na_2R + CaSO_4 \rightleftharpoons CaR + Na_2SO_4$$

where R is a complex aluminosilicate ion $[Al_2Si_2O_8 \cdot nH_2O]^{2-}$.

High-molecular synthetic organic materials, *ion-exchange resins*, are also used to soften water. Cation-exchange resins contain active groups $-SO_3H$, $-COOH$, or $-OH$, in which the hydrogen atom can be replaced by a cation. The active groups of anion-exchange resins are basic $-NH_2$, $=NH$, and $\equiv N$. The OH groups that form on the surface of the resin during its hydration serve as exchange anions. 'Distilled' water can be obtained by passing natural water through a system of cation and anion exchangers:

$$\text{cation exchange: } 2RH + Ca^{2+} = R_2Ca + 2H^+$$

$$\text{anion exchange: } 2ROH + SO_4^{2-} = R_2SO_4 + 2OH^-$$

where R is a complex organic radical.

Apart from their use to soften and desalinate water, ion exchangers are widely employed in hydrometallurgy to recover noble, nonferrous, and rare metals (Ag, Cu, Ni, Co, etc.), and to separate elements similar in chemical properties. Ion exchange is also extensively used in analytical chemistry.

CHAPTER 9

Group I *s* Elements

Group I *s* elements are the alkali metals lithium Li, sodium Na, and the elements of the potassium subgroup, namely potassium K, rubidium Rb, caesium Cs, and francium Fr. The main characteristics of these elements are given below:

	$_3$Li	$_{11}$Na	$_{19}$K	$_{37}$Rb	$_{55}$Cs	$_{87}$Fr
Atomic mass	6.94	22.99	39.1	85.47	132.9	[223]
Valence electrons	(2)$2s^1$	(8)$3s^1$	(8)$4s^1$	(8)$5s^1$	(8)$6s^1$	(8)$7s^1$
Metallic radius, nm	0.155	0.189	0.236	0.248	0.268	0.280
Ion E^+ radius, nm	0.068	0.098	0.133	0.149	0.165	0.175
Enthalpy of hydration, ΔH_{hydr} of E^+, kJ/mol	—500	—390	—305	—280	—246	—
Ionisation energy, eV:						
$E^0 \rightarrow E^+$	5.39	5.14	4.34	4.18	3.89	3.98
$E^+ \rightarrow E^{2+}$	75.4	47.3	31.8	27.5	25.1	—

	$_{3}Li$	$_{11}Na$	$_{19}K$	$_{37}Rb$	$_{55}Cs$	$_{87}Fr$
Abundance, mole per cent	0.02	2.4	1.4	7×10^{-3}	9.5×10^{-9}	—
Natural isotopes	^{7}Li (92.70%) ^{6}Li (7.30%)	^{23}Na (100%)	^{39}K (93.10%) ^{41}K (6.88%) ^{40}K (0.02%, β-rad.)	^{85}Rb (72.15%) ^{87}Rb (27.85%, β-rad.)	^{133}Cs (100%)	—

The atoms of these elements have only one valence electron. Compared with the elements of other subgroups, they have lower first ionisation energies, while their atoms and ions are the largest. Thus metallic character is most strongly expressed in the alkali metals. Since their second ionisation energy differs greatly from the first, they have a +1 oxidation state. Compounds in which their oxidation state is −1 have also been obtained for some of them. They exist in these compounds as anions E^-. The probability of their existence is explained by the electron affinity of the atoms of the alkali metals (see Table 6).

9.1. Lithium

Lithium Li has a higher ionisation energy than the other alkali metals, and the smallest atom and ion. In its properties it resembles magnesium (the diagonal resemblance in the periodic system).

Ionic bonding is most characteristic of lithium so that its coordination number, in contrast to the other second period elements, is higher than four. At the same time, because of its comparatively small ion, lithium has a high energy of solvation, and forms a covalent bond in lithium-organic compounds.

Lithium is quite abundant in the crust (0.002 mole per cent). Natural lithium is a mixture of two stable isotopes, namely ^{6}Li (7.3 per cent) and ^{7}Li (92.7 per cent). Radioactive isotopes have been obtained artificially. The most important lithium minerals are *spodumene* $LiAl(SiO_3)_2$, *amblygonite* $LiAl(PO_4)F$, and *lepidolite* $Li_2Al_2(SiO_3)_3(F,OH)_2$.

The simple substance. Lithium is a soft, silvery white metal (m.p. 179 °C, b.p. 1350 °C), and is the lightest of all metals (density, 0.534 g/cm^3).

It is highly active chemically, reacts with oxygen and nitrogen at normal temperatures, and is therefore soon oxidised in air, forming dark grey reaction products (Li_2O and Li_3N). It ignites at temperatures above 200 °C. In an atmosphere of fluorine and chlorine, and also in vapours of bromine and iodine, it ignites spontaneously in normal conditions. When heated, it reacts directly with sulphur,

carbon, hydrogen, and other nonmetals. When strongly heated, it burns in CO_2.

Lithium reacts with metals to form intermetallic compounds. With magnesium, aluminium, zinc, and certain other metals, it also forms solid solutions, in which the constituents are soluble in each other to a limited extent. Because it differs markedly from the other alkali metals in atomic radius, it yields eutectic mixtures with them.

Lithium is used for alloying metals, imparting valuable physical and chemical properties to them. Aluminium alloys, for example, containing up to 1 per cent Li, have high mechanical strength and resistance to corrosion. The addition of 2 per cent Li to commercial copper increases its electrical conductivity, and so on.

Although lithium is inferior in chemical activity to certain metals, its standard electrode potential is the most negative ($E^\circ_{298} = -3.05$ V), because of the high enthalpy of hydration of the Li^+ ion, which makes for a much greater displacement of equilibrium

$$Li\ (s) \rightleftarrows Li^+\ (sol) + e^-$$

toward ionisation of the metal than with the other alkali metals. For weakly solvating solvents (e.g. salt melts) its standard potential corresponds to its lower chemical activity in the alkali metal series.

Lithium decomposes water vigorously, displacing hydrogen from it, and reacts even more readily with acids.

Lithium is obtained by electrolysis of a molten eutectic LiCl—KCl mixture. It is stored in sealed vessels under a layer of vaseline or paraffin wax.

A very important field of application of lithium is in nuclear power engineering, in which it is used as a source of tritium

$$^6_3Li + ^1_0n = ^3_1H + ^4_2He$$

and as a coolant in reactors.

Compounds of lithium(I). The binary compounds of lithium are colourless crystalline salts or salt-like compounds that resemble derivatives of calcium and magnesium in chemical nature, solubility, and character of hydrolysis: LiF, Li_2CO_3, Li_3PO_4, etc., are poorly soluble in water.

Peroxide compounds are not characteristic of lithium, though a few are known: viz., the peroxide Li_2O_2, persulphide Li_2S_2, and percarbide Li_2C_2.

Lithium *oxide* Li_2O is a white solid obtained by interaction of the simple substances; it reacts actively with water to form a hydroxide, and forms salts with acids and acidic and amphoteric oxides.

The *hydroxide* LiOH is colourless, very hygroscopic, and soluble in water. It is a strong base ($K_b = 6.75 \times 10^{-1}$), but is inferior in strength and solubility to the hydroxides of the other Group I *s* ele-

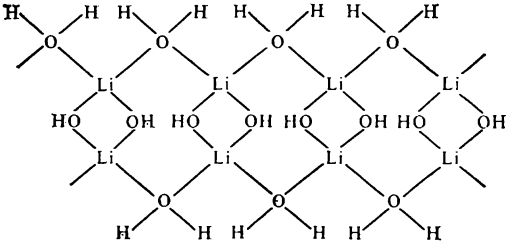
ments. When calcined, LiOH decomposes (unlike the hydroxides of other alkali metals):

$$2LiOH\ (c) \rightleftharpoons Li_2O\ (c) + H_2O\ (l), \quad \Delta G^\circ_{298} = 85\ kJ$$

LiOH is prepared by electrolysing aqueous solutions of LiCl. It is used as an electrolyte in storage batteries.

The aquo complexes of Li(I) are less stable than those of Be(II). No separate aquo ions have been discovered in existing crystal hydrates.

The water molecules in certain of the crystal hydrates are involved in the formation of bridge bonds. In $LiOH \cdot H_2O$ (monoclinic lattice), for instance, Li is surrounded by four oxygen atoms (two from the OH groups and two from the H_2O molecules), forming a distorted tetrahedron. Pairs of tetrahedra are joined by common edges (through the O atoms of the OH groups). Neighbouring pairs of tetrahedra are joined by common apexes (through the O atoms of H_2O) and form an endless $LiOH \cdot H_2O$ chain:



The chains are held together by hydrogen bonds.

In the crystal of $LiClO_4 \cdot 3H_2O$, each Li^+ ion is at the centre of an octahedron of H_2O molecules, but each water molecule belongs to two such octahedra, forming hexagonal columns of $[Li_2(OH_2)_6]^{2+}$ with ClO_4^- ions between them.

When lithium salts react (mutually crystallise or fuse) with similar compounds of other alkali metals, eutectic mixtures are formed, like $LiNO_3—KNO_3$ (m.p. 132 °C), $LiNO_3—NaNO_3—KNO_3$ (m.p. 120 °C), LiCl—KCl (m.p. 350 °C), etc. Double compounds, e.g. $\overset{+1}{M}LiSO_4$, $Na_3Li(SO_4)_2 \cdot 6H_2O$, and solid solutions are produced much less frequently.

Melts of salts and their mixtures form a very interesting, important class of nonaqueous solvents that dissolve most metals, forming intensely coloured solutions which are very strong reducing agents. The dissolved metals are either in the atomic state, or in the form of solvated ions of an unusually low oxidation state (Al^+, Ca^+, Be^+). The phenomenon is very important for many electrometallurgical and metallothermic processes, in metal refining, and in chemical synthesis.

Compounds dissolved in molten salts are ionised to form solvated ions. When $CoCl_2$, for example, is dissolved in the molten eutectic mixture $LiNO_3—KNO_3$, a solvated ion $[Co(NO_3)_6]^{4-}$ is formed, and KCl is added to the solution, a $[CoCl_4]^{2-}$ ion is formed. The reactions in molten salts may or may not involve a change in oxidation state.

Some minerals and artificial compounds of lithium (the aluminate, titanate, carbonate, silicate, molybdate, etc.) are used in the making of enamels, special glasses transparent to ultraviolet rays, and so on. Lithium forms organometallic compounds, which also makes it important in modern organic synthesis.

9.2. Sodium

Sodium is one of the most abundant elements (2.4 mole per cent). It has been discovered in the solar atmosphere and interstellar space. Its most important minerals are *rock salt*, *halite* NaCl, *mirabilite* or *Glauber's salt* $Na_2SO_4 \cdot 10H_2O$, *cryolite* Na_3AlF_6, *borax* $Na_2B_4O_7 \times \times 10H_2O$, etc. In combination with other elements it forms part of many natural silicates and aluminosilicates. There are immense quantities of sodium salts in the hydrosphere of the Earth (about 1.5×10^{16} tonnes).

Plant and animal organisms contain sodium compounds, mainly NaCl in the case of animals. Na^+ ions constitute about 0.32 per cent of human blood, 0.6 per cent of bone, and 0.6 to 1.5 per cent of muscle.

The simple substance. Sodium is a light (density 0.97 g/cm^3), soft, silvery white metal with comparatively low melting point (97.8°C) and boiling point (883 C).

Chemically it is most active. In air it oxidises immediately, forming friable oxidation products. In normal conditions it ignites spontaneously in fluorine and chlorine media. When slightly heated it reacts vigorously with liquid bromine, sulphur, iodine, hydrogen, etc.

Sodium forms intermetallic compounds with many metals; with tin, for example, it gives a series of compounds, viz., $NaSn_6$, $NaSn_4$, $NaSn_3$, $NaSn_2$, NaSn, Na_2Sn, Na_3Sn, etc. With some metals it produces solid solutions. The eutectic alloy containing 24 per cent Na and 76 per cent K is a liquid in normal conditions (f.p. —12.6 °C).

Sodium is used in metallothermy. Metallic sodium and its liquid alloy with potassium are employed in organic synthesis. Sodium amalgam is often used as a reducing agent. Sodium is also used as a heat-transfer medium in nuclear power installations, in the valves of aircraft engines, and in chemical processes where uniform heating within a range of 450 °C to 650 °C is required.

Sodium is obtained by electrolysis of molten NaCl (less frequently NaOH). When obtained from NaCl (m.p. 800 °C), the melting point of the electrolyte is lowered to 575-585 °C by adding KCl, $CaCl_2$, NaF, or other salts. Sodium is stored in sealed vessels or under kerosene.

Compounds of sodium(I). Ionic compounds are most characteristic of sodium(I). They have a crystalline structure and are more or

less high-melting; in the molten state they are electrolytes, and are readily soluble in water. A few derivatives with complex anions, e.g. the hexahydroxystibate(V), $Na[Sb(OH)_6]$, are barely soluble. Sodium bicarbonate (unlike the carbonate) is comparatively insoluble in water.

Since the polarising action of the Na^+ ion is insignificant, complex compounds are not characteristic. Even sodium aquo complexes are unstable so that most sodium salts do not form crystal hydrates. Crystal hydrates like $Na_2SO_4 \cdot 10H_2O$, $Na_2CO_3 \cdot 10H_2O$, etc., are relatively stable and are tectohydrates (see p 262).

The formation of peroxide compounds is more characteristic of sodium than of lithium. Thus, unlike lithium, it reacts with oxygen to form not an oxide but sodium peroxide:

$$2Na\ (c) + O_2\ (g) = Na_2O_2\ (c), \quad \Delta G^\circ_{298} = -447\ kJ$$

Sodium *monoxide* Na_2O is obtained indirectly by reducing Na_2O_2 by sodium metal. An unstable *ozonide* NaO_3 and *superoxide* NaO_2 are also known. *Persulphides*, Na_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5, are obtained by fusing sodium with sulphur.

Sodium chloride, sodium hydroxide, the sodium carbonates, and many other derivatives are very important commercially.

Sodium *chloride*, which occurs in nature in huge deposits, is the basic material for many important industrial processes, such as the production of sodium metal, sodium hydroxide, soda, chlorine, etc.

Sodium *hydroxide* (*caustic soda*) is used in huge quantities in various branches of industry, mainly in the production of soap, dyes, cellulose, etc. It is a very strong base ($K_b = 5.9$), obtained either by electrolysis of aqueous solutions of NaCl, or chemically.

One of the commonest chemical methods of producing NaOH is the *lime method* based on the interaction of a solution of soda and slaked lime

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$$

The equilibrium of the reaction is displaced toward the formation of NaOH because of the poor solubility of $CaCO_3$. The soda so obtained becomes caustic (Greek *kaustikos* to burn), hence the name for NaOH.

Sodium *carbonates* are used in many industries, viz., the chemical, soap, paper, textile, food and other industries. They are produced either as Na_2CO_3 (*soda ash*) (or the *crystal hydrate* $Na_2CO_3 \cdot 10H_2O$), or as sodium hydrocarbonate $NaHCO_3$ (*baking soda*).

The main method of producing baking soda is the ammonia-chloride process, based on the reaction

$$NaCl + NH_4HCO_3 \rightleftharpoons NaHCO_3 + NH_4Cl$$

the equilibrium of which is displaced toward the hydrocarbonate because of its comparative insolubility. Solubility curves of the salts in this system are shown in Fig. 201.

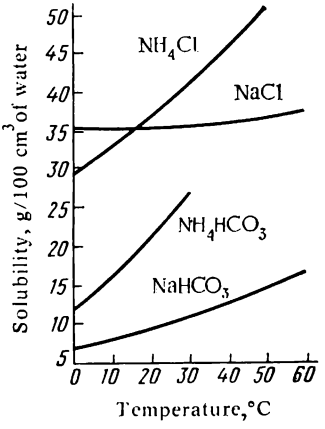


Fig. 201. Solubility of salts in water forming an NaCl + + $NH_4HCO_3 \rightleftarrows NaHCO_3$ + + NH_4Cl system

Soda Na_2CO_3 can also be obtained by reducing sodium sulphate by carbon in the presence of calcium carbonate:

$$Na_2SO_4\ (c) + 2C\ (graphite) + CaCO_3\ (c) = CaS\ (c) + Na_2CO_3\ (c) + 2CO_2\ (g)$$

$$\Delta H^\circ_{298} = 190\ kJ, \quad \Delta S^\circ_{298} = 370\ J/K$$

$$\Delta G^\circ_{298} = 81\ kJ$$

Since the reaction is endothermic, but proceeds with an increase in the system's entropy, heating is required to carry on the process.

9.3. Potassium Subgroup

The elements of the potassium subgroup, viz., potassium proper K, rubidium Rb, caesium Cs, and francium Fr, are the most typical metals, cationogens, their metallic character increasing with atomic number. Compounds with predominantly ionic bonds are most characteristic. Owing to the ions' low polarising action (low charge, stability of electron structure, and large size), complexation with inorganic ligands is not characteristic of K^+, Rb^+, Cs^+, and Fr^+, and even crystal hydrates are almost unknown for them.

The most important potassium minerals are *sylvite* KCl, *sylvinite* $NaCl \cdot KCl$, *carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$, and *kainite* $KCl \cdot MgSO_4 \times 3H_2O$.

Rubidium and caesium occur in natural potassium minerals. Francium is radioactive and has no stable isotopes. It was discovered in 1939 in products of the radioactive decay of uranium, in which it occurred in minute quantities (4×10^{-28} g per gram of natural uranium). Francium is now obtained artificially; the isotope with the longest life ^{212}Fr ($T_{1/2}$ = 20 min) is formed by bombarding uranium with protons:

$$^{238}U\ (p,\ 6p21n)^{212}Fr$$

Because of the short half-life of its isotopes, it is impossible to accumulate appreciable quantities of francium; for that reason its properties have not been adequately studied.

The simple substances. Potassium and its analogues are lustrous, silvery-white metals (except caesium, which is golden yellow) with

a body-centred lattice (like Li and Na). Their main physical constants (compared with those of lithium and sodium) are as follows:

	Li	Na	K	Rb	Cs
Density, g/cm³	0.53	0.97	0.85	1.5	1.9
Hardness (diamond = 10)	0.6	0.4	0.5	0.3	0.2
S°_{298}, J/K·mol	28.6	51.6	71.5	76.2	84.4
Heat capacity ($H_2O = 1$)	0.83	0.29	0.17	0.08	0.05
Electrical conductivity	11	21	14	8	5
$\Delta H^\circ_{subl.\ 298}$, kJ/mol	159.3	92.0	90.4	82.1	78.2
M. p., °C	180	98	63	39	29
B. p., °C	1330	900	766	700	685
E°_{298} $E^+ + e^- = E$, V (sol)	—3.05	—2.71	—2.92	—2.93	—2.92
$E^+ + e^- = E$, V (melt)	—2.1	—2.43	—2.61	—2.74	—2.91

As will be seen from the table, the density of K, Rb, and Cs is low (potassium, like Li and Na, is lighter than water) and their melting and boiling points not high. The metals themselves are very soft and can easily be cut with a knife. In the transition from lithium to sodium and on to potassium, most of the constants, it should be noted, change quite abruptly.

Potassium and its analogues are very reactive. Potassium rapidly oxidises in the air to form friable reaction products; caesium and rubidium ignite spontaneously. K, Rb, and Cs ignite spontaneously in fluorine and chlorine in normal conditions, and react with liquid bromine with a strong explosion. Potassium and its analogues react readily with hydrogen, sulphur, and other nonmetals when heated. With metals they form mainly intermetallic compounds.

Potassium and its analogues are at the very beginning of the electromotive series. Potassium reacts with water, liberating hydrogen, which ignites spontaneously; rubidium and caesium react explosively with water.

These metals readily lose electrons when heated or illuminated, and for that reason are valuable materials for making photoelectric cells.

Industrially potassium is reduced with sodium metal from the molten hydroxide or chloride. Rubidium and caesium are obtained either by metallothermic methods or thermal decomposition of their compounds. Potassium and its analogues are stored in sealed vessels. Potassium can also be stored in kerosene.

Compounds of potassium(I), rubidium(I), and caesium(I). The derivatives of potassium and its analogues are mainly salts and salt-like compounds, very similar to the corresponding compounds of sodium in composition, crystal structure, solubility, and character of solvolysis.

The crystalline compounds of the alkali metals have high coordination numbers. Thus, the EH hydrides have a structure of NaCl type, and the halides EHal of NaCl and CsCl type. The oxides E_2O, sulphides E_2S, selenides E_2Se,

and tellurides E_2Te of potassium and rubidium (and also of Li and Na) have a structure of the antifluorite type (Fig. 202), i.e. tetrahedral-cubic coordination of atoms.

In accordance with the elements' increasing chemical activity in the K—Rb—Cs series, the tendency to form peroxide compounds increases as well. Thus, in contrast to lithium, which burns in air to give the oxide, and sodium which yields a peroxide in the same

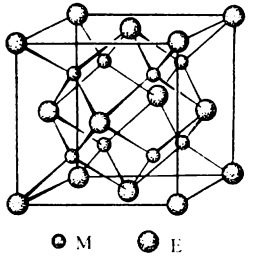


Fig. 202. Crystal lattice of M_2O (antifluorite type)

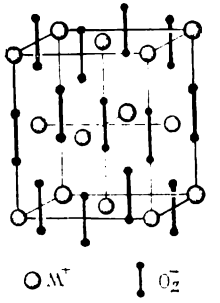


Fig. 203. Crystal lattice of MO_2 superoxides

conditions, potassium, rubidium and caesium form *superoxides* EO_2 when burnt (Fig. 203). The *peroxides* E_2O_2 (which are less stable than Na_2O_2) can also be obtained indirectly.

Peroxides and superoxides are strong oxidants, and easily decomposed by water, and even more so by dilute acids:

$$2KO_2 + 2H^+ = 2K^+ + H_2O_2 + O_2$$

The *ozonides* EO_3 are even stronger oxidants. They are formed by the action of ozone on solid hydroxides:

$$4KOH + 4O_3 = 4KO_3 + O_2 + 2H_2O$$

Ozonides gradually break down in storage in normal conditions:

$$2KO_3 = 2KO_2 + O_2, \quad \Delta G^\circ_{298} = -86 \text{ kJ}$$

in water they decompose rapidly, liberating oxygen

$$4KO_3 + 2H_2O = 4K^+ + 4OH^- + 5O_2$$

Persulphides (polysulphides) of potassium and its analogues can be obtained by boiling sulphides with excess sulphur (or by fusing dry sulphides with sulphur). The stability of the persulphides also increases in the K—Rb—Cs series. All members of the E_2S_n series (up to $n = 6$) have been obtained and studied for them (for Na up to $n = 5$, and for Li up to $n = 2$).

The *oxides* (white K_2O, yellow Rb_2O, and orange Cs_2O) are very reactive (like Na_2O), interacting vigorously with water to form

hydroxides. The increasing chemical activity in the series Li_2O—Na_2O—K_2O—Rb_2O—Cs_2O will be seen from the changes in the Gibbs' energy in the reaction

$$1/2E_2O\ (c) + 1/2H_2O\ (g) = EOH\ (c)$$

which is —47 kJ/mol for LiOH, and —111 kJ/mol for CsOH. This example also illustrates the considerable changes in properties of compounds in the transition from Li to Na and from Na to K.

E_2O can be obtained by reducing EO_2 by metals:

$$KO_2 + 3K = 2K_2O$$

The EOH *hydroxides* are colourless and very hygroscopic. Like NaOH, they sublime when heated without decomposition. The hydroxides are readily soluble in water, liberating much heat. Aqueous solutions of EOH (like NaOH solutions) are almost completely ionised and are the strongest bases, i.e. the *alkalis* KOH, RbOH, and CsOH. Potassium hydroxide KOH (*caustic potash*) is more important commercially than RbOH or CsOH. It is obtained by electrolysis of an aqueous solution of KCl.

In contrast to similar compounds of Li^+ and Na^+, the oxychlorates(VII) $EClO_4$, chloroplatinates(IV) E_2PtCl_6, nitritocobaltates(III) $E_3[Co(NO_2)_6]$, and certain others are barely soluble.

The most important of the many derivatives of potassium and its analogues are those of potassium itself. About 90 per cent of the potassium salts mined are used as fertilisers (as KNO_3, KCl, K_2SO_4, etc.). Potassium compounds are also used in the manufacture of glass, soap, etc. Compounds of potassium, rubidium, caesium, and francium are used in medicine.

CHAPTER 10

Group VIII *s* and *p* Elements

The main subgroup of Group VIII comprises helium He, neon Ne, argon Ar, and the elements of the krypton subgroup, viz., krypton Kr itself, xenon Xe, and radon Rn. Their atoms have a completed configuration of the outer electron layer $1s^2$ (He) and ns^2np^6.

	$_{2}$He	$_{10}$Ne	$_{18}$Ar	$_{36}$Kr	$_{54}$Xe	$_{86}$Rn
Atomic mass	4.0026	20.984	39.948	83.80	131.30	[222]
Valence electrons	$1s^2$	$(2)2s^22p^6$	$(8)3s^23p^6$	$(18)4s^24p^6$	$(18)5s^25p^6$	$(18)6s^26p^6$
Atom E radius, nm	0.122	0.160	0.192	0.198	0.218	0.22
Ionisation energy $E^0 \rightarrow E^+$, eV	24.59	21.57	15.76	14.00	12.13	10.75
Abundance, mole per cent	5×10^{-4}	1.8×10^{-3}	9.3×10^{-1}	1.1×10^{-4}	8.6×10^{-6}	6×10^{-20}

The molecules of these elements are therefore monatomic. In normal conditions, the simple substances of Group VIII *s* and *p* elements are gases, known as the *noble* or *inert* gases.

10.1. Helium

Compared with the other elements, helium He has the highest ionisation energy of its atom (24.59 eV). The special stability of its electron structure distinguishes it from all other chemical elements.

Helium is very much like hydrogen in physical properties. Because of its infinitesimal polarisability, helium has the lowest boiling point (—269 °C) and freezing point (—272 °C at 2.5×10^6 Pa).

Helium dissolves less than other gases in water and other solvents; less than ten millilitres can be dissolved in a litre of water at 0 °C, which is less than about two and a half times the solubility of hydrogen. HCl is 51 000 times more soluble than He.

In normal conditions helium is chemically inert, but when its atoms are strongly excited it can form molecular ions He_2^+ $[(\sigma_s)^2(\sigma_s^*)^1]$. In normal conditions these ions are unstable, capture the missing electron, and break down into two neutral atoms. Ionised HeH^+ $[(\sigma_s)^2]$ molecules can also be formed.

Helium comes next after hydrogen as regards abundance in the Universe. It consists of two stable isotopes, ^4He and ^3He. Spectrum analysis indicates its presence in the atmosphere of the Sun and stars, and in meteorites. The accumulation of ^4He nuclei in the Universe is due to the thermonuclear reactions that are the source of solar and stellar energy

$$4\,{}^1_1H = {}^4_2He + 2\beta^+ + 2\tilde{\nu}$$

Helium accumulates in the Earth's crust through alpha decay of radioactive elements, and is contained, dissolved, in minerals and native metals. The ^3He isotope is formed by nuclear reactions induced by cosmic radiation, for example

$${}^{14}_7N + {}^1_0n = {}^{12}_6C + {}^3_1T;\ {}^3_1T = {}^3_2He + \beta^-$$

The helium nuclei (alpha particles) are quite stable and are widely used in nuclear reactions.

Helium is mainly obtained industrially from natural gases by intense cooling. Being the substance with the lowest boiling point, it remains a gas when all others are frozen.

Gaseous helium is widely used to create an inert atmosphere for welding metals, in preserving foodstuffs, etc. Liquid helium is used in the laboratory as a refrigerant for work in low-temperature physics.

10.2. Neon

Neon, like helium, has a very high ionisation potential (21.57 eV) and so does not form valence compounds.

The main difference between neon and helium is that the neon atom is relatively more polarisable, i.e. it has a greater tendency to form intermolecular bonds.

Neon has a very low boiling point (—245.9 °C) and freezing point (—248.6 °C), surpassed only by helium and hydrogen. Its solubility and absorption capacity are rather better than those of helium.

Neon, like helium, forms Ne_2^+ molecular ions, when strongly excited:

$$[\sigma_s]^2 [\sigma_s^*]^2 [\sigma_z]^2 [\pi_{x,y}]^4 [\pi_{x,y}^*]^4 [\sigma_z^*]^1$$

It is obtained together with helium as a by-product of the liquefaction and fractionation of air, being separated from helium by either adsorption or condensation. The adsorption technique is based on its capacity (in contrast to helium) to be adsorbed on activated charcoal cooled by liquid nitrogen. The condensation technique is based on freezing neon by cooling the mixture with liquid hydrogen.

Neon is widely used in electronics for filling voltage stabilisers, photoelectric cells, and other instruments. Various types of neon lamps with a characteristic red glow are used in lighthouses and other illuminating equipment, advertising signs, etc.

Natural neon is a mixture of three stable isotopes, viz., ^{20}Ne, ^{21}Ne, and ^{22}Ne.

10.3. Argon

The valence shell of argon (like that of neon) has eight electrons. Because of the high stability of the atom's electron structure (ionisation energy, 15.76 eV) valence compounds of argon have not been obtained. Because of the relatively large size of its atom (molecule), it has a greater tendency to form intermolecular bonds than helium and neon. For that reason the simple substance has higher freezing and boiling points (—189.3 °C and —185.9 °C respectively). It is also adsorbed better.

Argon forms molecular inclusion compounds, clathrates, with water, phenol, toluene, and certain other substances. Argon hydrate of average $Ar \cdot 6H_2O$ composition is a crystalline compound decomposing at —42.8 °C at atmospheric pressure. It can be obtained by the direct interaction of argon and water at 0 °C and a heightened pressure of the order of 1.5×10^7 Pa. With H_2S, SO_2, CO_2, and HCl it forms double hydrates, i.e. mixed clathrates.

Argon is obtained during the fractionation of liquid air, and also from the waste gases of ammonia synthesis. It is used in metallurgical and chemical processes where an inert medium is required (arc-welding of aluminium and aluminomagnesium alloys), in fluorescent and incandescent lamps and discharge tubes, in electrical engineering, nuclear power engineering (ionisation counters and chambers), and so on.

Argon is the most abundant of all the inert gases of Earth, its content in the atmosphere being 0.93 volume per cent. Natural argon is a mixture of three stable isotopes, viz., ^{40}Ar (99.600 per cent), ^{38}Ar (0.063 per cent) and ^{36}Ar (0.337 per cent). In natural conditions ^{40}Ar is produced during the decay of ^{40}K as a result of electron capture from the *K* shell (i.e. the 1*s* electron of potassium):

$$^{40}_{19}K + e^- \rightarrow {}^{40}_{18}Ar$$

10.4. The Krypton Subgroup

Krypton Kr, xenon Xe, and radon Rn have lower ionisation energies than the typical Group VIII elements. Therefore they yield compounds of ordinary type. Xenon, for example, has oxidation states of +2, +4, +6, and +8, and resembles iodine (which is close to it in ionisation energy) in the character of its compounds.

The elements of the krypton subgroup differ from the other noble gases by their larger atoms (molecules) and greater polarisability, which increases as follows in the series He—Ne—Ar—Kr—Xe 1 : 2 : 3 : 12 : 20, i.e. xenon is 20 times more polarisable than helium. The increasing polarisability has its effect on strengthening intermolecular interactions, which in turn affects the boiling and melting points of the simple substances:

	He	Ne	Ar	Kr	Xe	Rn
r_E, nm	0.122	0.160	0.192	0.198	0.218	0.22
B. p., °C	—269	—246	—186	—153	—108	—62
M. p., °C	—272*	—249	—189	—157	—112	—71
Solubility in 1 litre of water at °C, ml	10	—	60	—	500	—

* at a pressure of 2.5×10^6 Pa.

The solubility of the gases in water and other solvents, their tendency to be adsorbed, etc., also increase in the He—Ne—Ar—Kr—Xe—Rn series. In the solid state, krypton, xenon, and radon, like Ne and Ar, have face-centred cubic lattices (see Fig. 66*a*).

The stability of the inclusion compounds increases through the He—Rn series. Thus, the temperature at which the dissociation pressure of the clathrates $Ar \cdot 6H_2O$, $Kr \cdot 6H_2O$, and $Xe \cdot 6H_2O$ reaches atmospheric pressure is —43 °C, —28 °C, and —4 °C respective-

ly. To obtain xenon hydrate at 0 °C, on the contrary, a pressure a little above atmospheric is sufficient. Hydrates of krypton, argon, and neon require pressures of 1.5×10^6, 1.5×10^7 and 3×10^7 Pa respectively. It can be thought that helium hydrate could be obtained if the pressure could be raised to the order of 10^8 Pa.

Other molecular compounds of a clathrate type besides hydrates have been obtained for the elements of the krypton subgroup (by B. A. Nikitin). The difference in the stability of their clathrate compounds is utilised to separate the noble gases. In industry, krypton is separated together with xenon during rectification of liquid air.

Krypton is used in electronics; a mixture with xenon is used to fill various lamps, and tubes. Radioactive radon is used in medicine (radon baths).

Compounds of krypton, xenon and radon. Most valence compounds of the noble gases are stable solids in normal conditions. As a rule they melt at temperatures above 100 °C; many easily sublimes.

All the numerous compounds of the noble gases are obtained from the corresponding fluorides, while the latter are obtained by direct synthesis from the simple substances. Xenon fluorides are formed with liberation of heat:

$$Xe\ (g) + F_2\ (g) = XeF_2\ (c), \quad \Delta H^\circ_{298} = -176\ kJ$$
$$Xe\ (g) + 2F_2\ (g) = XeF_4\ (c), \quad \Delta H^\circ_{298} = -252\ kJ$$
$$Xe\ (g) + 3F_2\ (g) = XeF_6\ (c), \quad \Delta H^\circ_{298} = -295\ kJ$$

Xenon burns in a fluorine atmosphere with a bright flame. The composition of the compounds thus formed depends on the composition of the initial mixture, and the duration and conditions of the reaction. The synthesis of krypton fluoride is more complicated and requires external energy. A general survey of compounds of the noble gases is given in Table 45.

It has been calculated that the transfer of p electrons of Kr and Xe atoms to other energy states requires much external energy. In order to excite the Xe atom from its $5s^25p^6$ ground state, for example, to the $5s^25p^56s^1$ and $5s^25p^55d^1$ states requires 795 and 963 kJ/mol, while excitation to the $5s^25p^45d^2$ and $5s^25p^45d^16s^1$ states requires 1758 and 1926 kJ/mol respectively. These high energy expenditures cannot be compensated during the formation of two-electron two-centre bonds.

The formation of compounds of elements of the xenon subgroup is explained by the concept of three-centre, four-electron, hypervalent bonds (see Fig. 139). Three three-centre molecular orbitals, viz., one bonding, one nonbonding and one antibonding orbital (Fig. 204) are formed in a linear molecule of XeF_2 by one $5p$ orbital of the Xe atom and two $2p$ orbitals of the F atom. Four electrons are involved

Table 45. **Compounds of Noble Gases**

Type of compound	Compounds at various oxidation states			
	+2	+4	+6	+8
Halides	KrF_2 XeF_2, $XeCl_2$ (RnF_2)	— XeF_4 (RnF_4)	— XeF_6 (RnF_6)	— — —
Oxides	—	—	XeO_3	XeO_4
Oxyfluorides	—	—	$XeOF_4$ XeO_2F_2	XeO_3F_2
Fluorine complexes*	$[XeF][MF_6]$ $[KrF][MF_6]$	$[XeF_3]$ $[MF_6]$ — —	$[XeF_5][MF_6]$ $[XeOF_3][MF_6]$ $Cs_2[XeF_8]$	$[XeOF_5][MF_6]$ — —
Salts of oxyacids	$Xe[ClO_4]_2$ $[XeF][NO_3]$	— —	— —	— —
Acids	—	—	H_2XeO_4	H_4XeO_6

* M = Pt, Ir, Os, Ru, Au, Nb, Ta, Sb.

in these three molecular orbitals, distributed in the bonding and nonbonding orbitals, so that a quite strong bond is formed as a

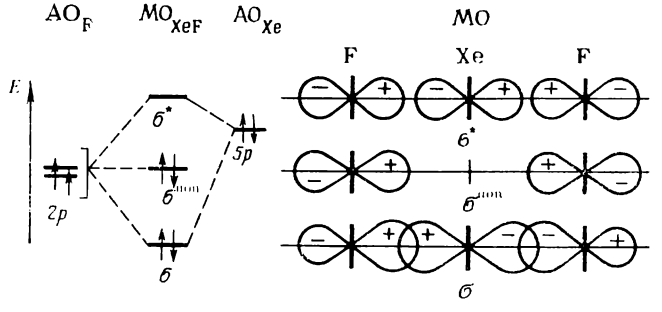


Fig. 204. Three-centre orbitals in the XeF_2 molecule

result. The nonbonding orbital is located for all intents and purposes in the fluorine atom. In the XeF_2 molecule, the charge is partly transferred from the Xe atom to the F atom and the latter's effective

charge becomes negative ($\delta_F \approx 0.5-$). Thus, only the most electronegative atoms (e.g. of fluorine or oxygen) can act as ligands in compounds of the noble gases. Furthermore, since the central atom acts as the donor of an electron pair, bond strength should, in general, decrease with increasing ionisation energy, which explains why the stability of xenon compounds is high while compounds of He, Ne and Ar are not known.

Since each $5p$ orbital of the xenon atom can form a linear fragment F—Xe—F, the structure of the square XeF_4 molecule (Fig. 51*j*) can be explained in a similar way.

The structure of XeF_2 crystal (m.p. 140 °C, density 4.32 kg/m³) and XeF_4 crystal (m.p. 114 °C, density 4.04 kg/m³) is shown in Fig. 205. The xenon hexafluoride XeF_6 is a white crystalline solid (m.p. 46 °C), stable at room tempera-

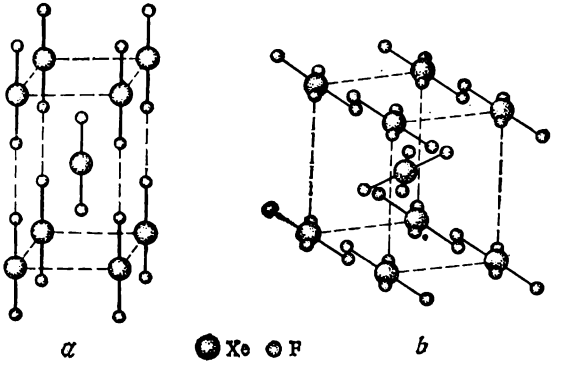


Fig. 205. Structure of XeF_2 and XeF_4 crystals

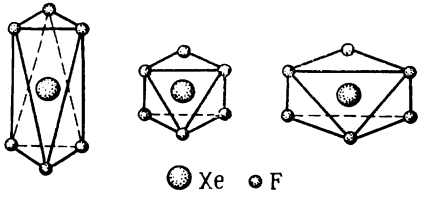


Fig. 206. Shapes of molecules of xenon hexafluoride

ture. Its molecule has a peculiar shape (Fig. 206) that differs from the octahedral molecules of most other hexafluorides. XeF_6 is highly active chemically and reacts with SiO_2:

$$SiO_2 + 2XeF_6 = 2XeOF_4 + SiF_4$$

Our survey indicates that the following pattern can be observed as the oxidation state of xenon increases: the basic character of similar compounds decreases while their acidic properties strengthen. Thus

XeF_2 is a basic compound and can form cation complexes, for example by interacting with pronouncedly acidic compounds like SbF_5 (or PtF_5, NbF_5, TaF_5, etc.):

$$XeF_2 + SbF_5 = [XeF][SbF_6]$$

Moreover, XeF_2 undergoes replacement to form salt-like compounds:

$$XeF_2 + HClO_4 = [XeF][ClO_4] + HF;$$
$$XeF_2 + 2HClO_4 = Xe[ClO_4]_2 + 2HF$$

In contrast to XeF_2 and XeF_4, the xenon(VI) fluoride has amphoteric properties. When XeF_6 reacts with more acidic fluorides, derivatives of a XeF_5^+ cation complex are formed, e.g. $[XeF_5][SO_3F]$. The interaction with more basic fluorides yields hepta- and octafluoroxenates(VI): e.g.

$$CsF + XeF_6 = Cs[XeF_7], \quad 2CsF + XeF_6 = Cs_2[XeF_8]$$

The fluoroxenates(VI) of caesium and rubidium are stable (decomposing at temperatures above 400 °C).

The existence of derivatives of the $XeOF_3^+$ cation complex (for example, $[XeOF_3][SbF_6]$) and of the $XeOF_5^-$ complex (e.g. $[NO][XeOF_5]$) indicates that xenon(VI) oxyfluoride $XeOF_4$ has both basic and acidic properties. The acidic nature of xenon(VI) oxide XeO_3 is shown by the existence of derivatives of the XeO_4^{2-} anion complex, i.e. the salts, oxyxenates(VI), that resemble oxysulphates(VI) in many respects.

Xenon trioxide XeO_3 is a white, nonvolatile, very explosive compound ($\Delta H_f^\circ = 402$ kJ/mol). The molecule has a trigonal pyramidal structure ($\angle XeOXe = 103°$, $d_{XeO} = 0.176$ nm). It is easily obtained by hydrolysis of XeF_6 or $XeOF_4$, or by oxidation-reduction (disproportionation) hydrolysis of XeF_4, for example by the action of damp air on them:

$$XeF_6 + H_2O = XeOF_4 + 2HF$$
$$XeOF_4 + 2H_2O = XeO_3 + 4HF$$
$$6XeF_4 + 12H_2O = 2XeO_3 + 4Xe + 3O_2 + 24HF$$

Xenon oxytetrafluoride $XeOF_4$ is a colourless liquid freezing at −28 °C. The molecule has a square pyramidal configuration.

The derivatives of xenon(VIII), i.e. the oxide XeO_4 and oxyfluoride XeO_3F_2, are predominantly acidic compounds.

The molecule of XeO_4 is tetrahedral with the Xe atom in the centre ($d_{XeO} = 0.16$ nm). It is obtained by the action of anhydrous sulphuric acid on barium oxyxenate(VIII) at room temperature:

$$Ba_2XeO_6 + 2H_2SO_4 = 2BaSO_4 + XeO_4 + 2H_2O$$

In normal conditions, XeO_4 is a gas that decomposes slowly into Xe, XeO_3, and O_2. In the solid state it explodes even at a temperature −40 °C.

The composition and the structure of the hexaoxyxenates(VIII) (called *perxenates* by analogy with periodates) fully agree with xenon's position in the fifth period. Like the other oxy ions of fifth period *p* elements XeO_6^{4-} has an octahedral structure with the Xe atom at the centre:

$$SnO_6^{8-} \quad SnO_6^{7-} \quad TeO_6^{6-} \quad IO_6^{5-} \quad XeO_6^{4-}$$

Xenon compounds are strong oxidants. The XeO_6^{4-} ion, for example, is a stronger oxidant in an acidic medium than MnO_4^- and fluorine (the standard electrode potential of the XeO_6^{4-}/Xe system is 3.0 V and of the F_2/F^- system 2.87 V). Practically all elements can be transferred to their highest oxidation state by the action of xenon compounds. (AuF_5 and BrF_7, for example, have been obtained by the action of XeF_2.)

Disproportionation reactions are also characteristic of xenon compounds: e.g.

$$4\overset{+6}{X}eF_6 + 18Ba(OH)_2 = 3Ba_2\overset{+8}{X}eO_6 + \overset{0}{X}e + 12BaF_2 + 18H_2O$$

The chemistry of the noble gases is being intensely studied and ways of employing them planned. Attempts are being made to trap the radioactive krypton and xenon liberated in nuclear reactors as fluorides. The fluorides are used as fluorinating and oxidising agents. The oxides of xenon present interest as explosives that leave no solid residue.

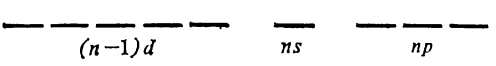
III

THE CHEMISTRY OF *d* ELEMENTS

CHAPTER 1

General Features

Another name for *d* elements is *transition* elements. They are located in the long periods of the periodic system between the *s* and *p* elements. A characteristic feature of them (see Table 3) is that in them the orbitals of the penultimate shell of the atom (*d* elements) are filled (rather than the outermost shell, as in *s* and *p* elements). The valence orbitals of *d* elements are nine orbitals similar to one another as regards energy, viz., one *ns* orbital, three *np* orbitals and five $(n-1)d$ orbitals:



One or two electrons are found in the outermost shell of *d* elements (*ns* state), while the other valence electrons are in an $(n-1)d$ state, i.e. in the penultimate shell. This structure of the electron shells of *d* elements determines several of their common properties. Their atoms have relatively low first ionisation energies. Their atoms are intermediate in size between those of the *s* and *p* elements of a given period. The simple substances of the transition elements are metals (the number of valence electrons in their atoms being much fewer than the number of orbitals).

1.1. Oxidation States of *d* Elements

These elements (with a few exceptions) have variable oxidation states. A +2 oxidation state (according to the number of the valence electrons) is characteristic of almost all *d* elements. The highest oxidation state of most of them corresponds to the number of the

group of the periodic system to which the element belongs, e.g. $\overset{+3}{Sc_2O_3}$, $\overset{+4}{TiO_2}$, $\overset{+5}{V_2O_5}$, $\overset{+6}{CrO_3}$, $\overset{+7}{Mn_2O_7}$, $\overset{+8}{(FeO_4)}$. In contrast to the subgroups of *s* and *p* elements, the stable oxidation state of *d* elements increases with their atomic number. Thus, no Fe(VIII) oxide is known, while OsO_4 is a stable compound ($\Delta G^\circ_{f,298} = -302$ kJ/mol).

Because of the variety of oxidation states oxidation-reduction processes are characteristic of the chemistry of *d* elements. For the same reason, almost every *d* element forms compounds that differ substantially in their acid-base properties: for example,

$Mn(OH)_2$	$Mn(OH)_3$	$Mn(OH)_4$	H_2MnO_4	$HMnO_4$
Medium strength base	Weak base	Amphoteric hydroxide	Strong acid	Very strong acid

1.2. Coordination Compounds of *d* Elements

The transition elements often form *coordination* compounds, among which the complex compounds of *d* elements are quite varied. It will be recalled that it is characteristic of coordination compounds not to have separate molecules of the compound in the structure of their crystal lattice (for example, NaCl, CoO, $K_4[Fe(CN)_6]$. Each atom (ion) in these compounds is surrounded by a certain number of ligands (atoms, ions, or groups of atoms). If the complex (the central atom and the surrounding ligands) does not decompose when passing into solution, the coordination compound is classed as a *complex*. Comparison of the structures of two coordination compounds CoO (NaCl structure type, see Fig. 69*a*) and $[Ni(NH_3)_6]Cl_2$ (see Fig. 68) indicates that the latter is a complex while CoO is not.

To explain the formation and properties of complex compounds we now employ the theory of valence bonds, crystal field theory, and the theory of molecular orbitals.

The description of complex compounds from the standpoint of valence bond theory will be found on p. 104. At present, however, this theory has lost its former importance in regard to complex compounds. While otherwise quite helpful, it does not explain many important properties of compounds in particular their absorption spectra, details of their magnetic properties, etc.

1.3. Description of Complex Compounds by Crystal Field Theory

Crystal field theory is based on the assumption that purely electrostatic interactions operate between a complexing agent and ligands (ionic bond). But unlike classical electrostatic views (see p 94), crystal field theory allows for the effect of the ligands' elec-

trostatic field on the energy state of the complexing agent's electrons.

Crystal field theory was first used to explain the properties of crystalline substances (hence its name), but it can equally be applied to any other system in which the interacting particles have a regular arrangement (e.g. to a separate complex).

Let us consider the main principles of crystal field theory from the example of single-nucleus complexes of *d* elements. As we know, the five *d* orbitals are arranged differently around the atomic nucleus.

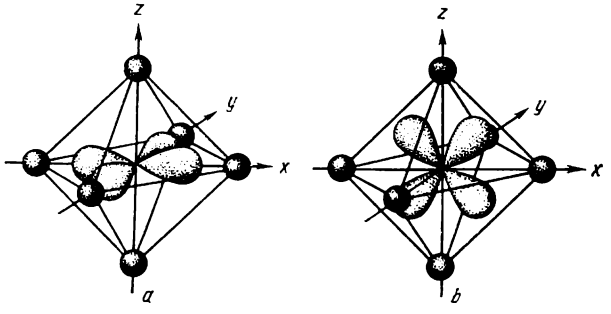


Fig. 207. (*a*) $d_{x^2-y^2}$ orbitals and (*b*) d_{xz} orbitals in an octahedral ligand field

The d_{z^2} orbital is concentrated along the *z* axis, the $d_{x^2-y^2}$ orbital along the *x* and *y* axes, while the d_{xy}, d_{xz}, and d_{yz} orbitals are concentrated along the bisectors of the inter-axial angles (see Fig. 7)*.

All five *d* orbitals of one and the same level in a free atom or ion have the same energy, i.e. are degenerate. If an ion of a *d* element comes into the centre of the sphere of an evenly distributed negative charge (a hypothetical case), all five electron clouds will be equally repelled. This repulsion of the *d* electrons from the sphere would excite the *d* level, but the degeneracy would not be removed.

A different picture will arise if the ion is put inside an octahedral, tetrahedral, or other surrounding (less symmetrical than a spherical one). Let us assume that there is a positive ion of a *d* element within an *octahedral* medium of negatively charged ions or polar molecules. In that case, the d_{z^2} and $d_{x^2-y^2}$ electrons are repelled more strongly from the ligands than the d_{xy}, d_{yz}, and d_{xz} electrons (Fig. 207). The energy of the *d* electrons in these conditions is different, being higher in the d_{z^2} and $d_{x^2-y^2}$ levels than in the d_{xy}, d_{xz}, and d_{yz} states. Thus, while the five *d* orbitals have the same energy in a free ion or an ion

* The d_{z^2} and $d_{x^2-y^2}$ orbitals are usually designated as d_γ while d_{xy}, d_{xz}, and d_{yz} orbitals are designated as d_ε.

placed in a spherical field, they form two groups (of two and three orbitals with different energies) in an octahedral field of ligands (Fig. 208).

The picture will be the opposite in a *tetrahedral* field; the d_{xy}, d_{xz}, and d_{yz} orbitals will then be closer to the ligands (Fig. 209). The

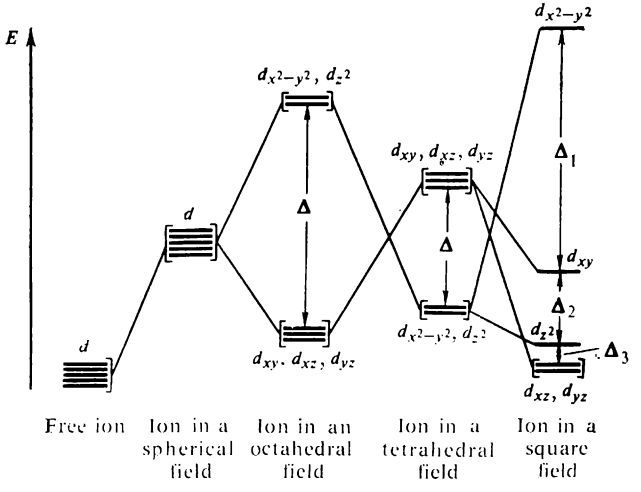


Fig. 208. The splitting of the *d* level in crystal fields of various symmetry

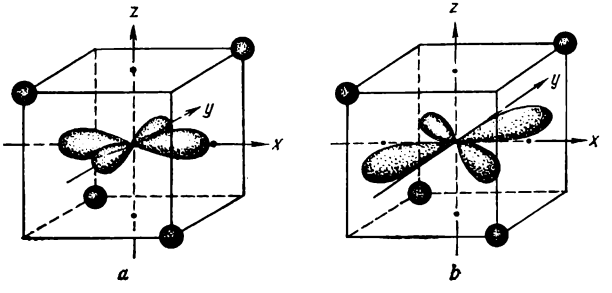


Fig. 209. (*a*) $d_{x^2-y^2}$ and (*b*) d_{xy} orbitals in a tetrahedral ligand field

d_{xy}, d_{yz}, and d_{xz} electrons will consequently experience greater electrostatic repulsion than the d_{z^2} and $d_{x^2-y^2}$ electrons, so that the d_{z^2} and $d_{x^2-y^2}$ orbitals will have lower energies, and the d_{xy}, d_{xz}, and d_{yz} orbitals higher ones (Fig. 208).

The energy difference of the *d* levels Δ is called the *splitting energy*. The parameter of the splitting of the *d* level depends on the

configuration of the complex, and the nature of both the ligand and the complexing agent. Figure 208 shows that the different spatial configurations of complexes correspond to different values of Δ, which is lower in a tetrahedral field; the resultant splitting parameter of a square field will be much higher than of the octahedral one. When the ligands and their distance from the complexing agent are identical, the value of Δ for a tetrahedral field will be 4/9th of that for an octahedral one ($\Delta_{tetr} = 4/9\Delta_{oct}$).

With one and the same central ion and configuration of complexes, the value of Δ will be higher when the field of the ligands is stronger. The ligands can be arranged in the following series according to their capacity to split the *d* shell: CO, $CN^- > NO_2^- > NH_3 > > NCS^- > OH_2 > OH^- > F^- > Cl^- > Br^- > I^-$. This series, known as the *spectrochemical series*, was discovered from experimental studies of the spectra of complexes and quantum-mechanical calculations.

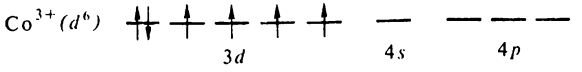
The degree of splitting of energy levels by a crystal field depends on the oxidation state of the central atom and the type of *d* electrons involved. The degree of splitting increases with the oxidation state of the *d* element (with increasing ion charge), since the ligands are closer to the central ion and hence cause greater splitting of the *d* orbital. The value of Δ for similar complexes increases markedly in the subgroups of *d* elements in the transition from the 4th period to the 5th, and especially to the 6th period, which is due to the greater distances between the 4*d* and 5*d* orbitals and the nucleus compared with 3*d* orbitals. This corresponds to a greater repulsion of the electrons and ligands, and accordingly to a higher degree of splitting of the 4*d* and 5*d* levels compared with the 3*d* level.

Low-spin and high-spin complexes. Crystal field theory gives a very simple explanation of the magnetic properties, spectra, and certain other properties of complexes. To understand these properties, we have to know the way the electrons are distributed in the *d* orbitals of the ion in the field of the ligands, which depends on the ratio of the splitting energy Δ and the energy of mutual repulsion of the electrons.

When the energy of interelectron repulsion is higher than the splitting energy, the five *d* orbitals are filled in succession, first with one electron, and then with a second. This is the case with a *weak field*. If the field is *strong*, and the splitting energy is higher than the mutual repulsion of electrons, the orbitals of lower energy are filled first, before those of higher energy begin to be filled.

Let us consider the example of the distribution of 3*d* electrons in the Co^{3+} ion during the formation of octahedral $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ complexes. In the free Co^{3+} ion ($3d^6$) electrons are

distributed as follows



It has been calculated that the repulsion energy of electrons in one and the same orbital is 251 kJ/mol for the Co^{3+} ion, and that the splitting energy of the 3*d* orbitals is 156 kJ/mol in the octahedral field of an F^- ion, and 265 kJ/mol in the field of H_3N molecules.

Thus, Δ is small in the field of the ion F^-, while the number of unpaired electrons in the orbitals of the split levels of Co^{3+} is the

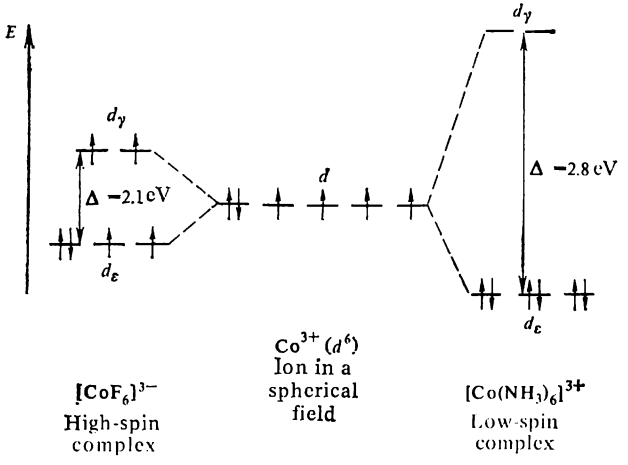


Fig. 210. Distribution of the *d* electrons of the Co^{3+} ion in $[CoF_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ octahedral complexes

same as in the free ion (Fig. 210). In the strong field generated by H_3N molecules, however, the splitting energy is higher, and it is more advantageous as regards energy when the *d* electrons of the Co^{3+} ion are arranged in lower *d* orbitals only.

The $[CoF_6]^{3-}$ ion can accordingly be called a *high-spin* complex (four unpaired electrons) and the $[Co(NH_3)_6]^{3+}$ ion a *low-spin* (or *spin-paired*) complex (no unpaired electrons).

Let us take another example. It can be shown that two octahedral complexes of Co^{2+} (d^7), viz., $[Co(OH_2)_6]^{2+}$ and $[Co(CN)_6]^{4-}$, are high-spin (three unpaired electrons) and low-spin (one unpaired electron) complexes respectively.

In accordance with the electron distribution in *d* orbitals, the complex $[Co(NH_3)_6]^{3+}$ is diamagnetic while the $[CoF_6]^{3-}$, $[Co(NH_3)_6]^{2+}$,

and $[Co(CN)_6]^{4-}$ complexes are paramagnetic (which has been proved experimentally).

As already pointed out, Δ increases for similar complexes in *d* element subgroups in the transition from the 4th period to the 5th, and especially to the 6th. For that reason, complexes of 4*d* and 5*d* elements are almost always low-spin ones.

The splitting parameter is usually determined from the absorption spectra of compounds. The quanta of light that excite electrons from lower *d* orbitals to higher ones, correspond to the visible region of the spectrum and the values of Δ lie within the limits of $1\ eV < \Delta < 4\ eV$, which explains why the compounds of *d* elements are usually coloured.

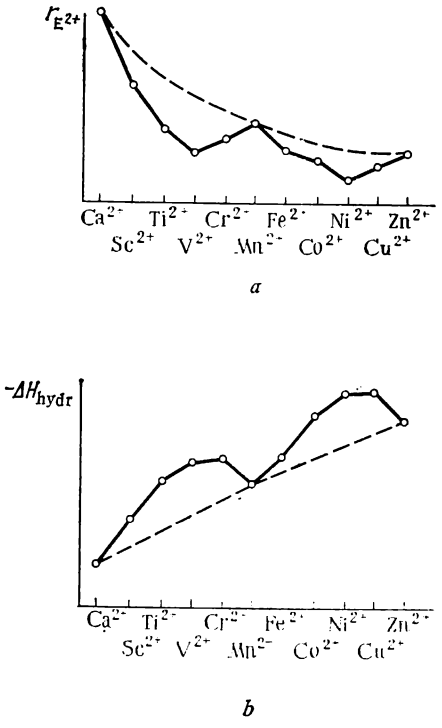


Fig. 211. Change in radius of (*a*) dipositive ions and (*b*) enthalpies of hydration in the Ca^{2+}—Zn^{2+} series

Crystal field theory explains many properties of *d* elements and their compounds. It can be extended to describe crystalline compounds. If we assume that a crystal consists of ions, then each ion of *d* elements will be found in the field of negative ions, which will cause splitting of the *d* level of the *d* element, which in turn will determine the magnetic properties, colour and other properties of its compounds.

Let us consider how *d* electron configuration affects the radius of a dipositive ion lying in an octahedral field of ligand ions in a crystal. The dependence of the ionic radii in the series from Ca^{2+} to Zn^{2+} on the element's atomic number is shown in Fig. 211. The electron configurations of the ions in this series are as follows:

Ca^{2+}	Sc^{2+}	Ti^{2+}	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}

If it were not for the crystal field effect, the ionic radii should decrease uniformly with increasing nuclear charge (atomic number of the element), as is shown in Fig. 211 by the broken curve connecting points corresponding to the spherically symmetrical ions Ca^{2+} (d^0), Mn^{2+} (d^5) and Zn^{2+} (d^{10}).

The actual radii of the ions (except Ca^{2+}, Mn^{2+}, and Zn^{2+}), however, lie below the broken line which can be explained by crystal field theory. The negative charge of the electron in the d_ε orbital is concentrated in the region between

the ligands (see Fig. 207*b*), while the electron density of the d_γ electron is displaced forward the ligands (Fig. 207*a*). Hence, the d_ε electrons shield the ion nucleus (screen it from the ligands) less than the d_γ electrons do. The appearance of an electron in a d_ε orbital therefore increases the attraction of the negatively charged ligand to the positively charged ion of the *d* element, and hence brings them closer to each other. This explains the diminishing effective radius in the series $Ca^{2+}(d^0)$ — $Sc^{2+}(d_\varepsilon^1)$ — $Ti^{2+}(d_\varepsilon^2)$ — $V^{2+}(d_\varepsilon^3)$ and $Mn^{2+}(d_\varepsilon^3 d_\gamma^2)$ — $Fe^{2+}(d_\varepsilon^4 d_\gamma^2)$ — — $Co^{2+}(d_\varepsilon^5 d_\gamma^2)$ — $Ni^{2+}(d_\varepsilon^6 d_\gamma^2)$.

The appearance of an electron in a d_γ orbital shields the nucleus of the ion better and prevents it from approaching the ligand, which causes a relative increase in the radius of ions in the series $V^{2+}(d_\varepsilon^3)$ — $Cr^{2+}(d_\varepsilon^3 d_\gamma^1)$ — $Mn^{2+}(d_\varepsilon^3 d_\gamma^2)$ and $Ni^{2+}(d_\varepsilon^6 d_\gamma^2)$ — $Cu^{2+}(d_\varepsilon^6 d_\gamma^3)$ — $Zn^{2+}(d_\varepsilon^6 d_\gamma^4)$.

This pattern explains the character of the variation in the hydration heats of ions in the Ca^{2+} — Zn^{2+} series (Fig. 211), since there heat of hydration depends on their radius (provided the charge is the same). The ion with the shortest radius (Ni^{2+}) has the maximum heat of hydration and the ion with the longest radius (Ca^{2+}) the minimum heat.

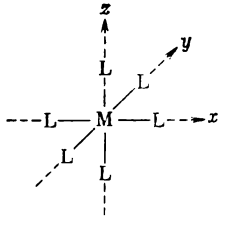
Since lattice energy, enthalpy of formation, Gibbs' energy of formation, etc., depend on the size of an ion, similar patterns can be observed in their variation in the series of *d* elements.

Crystal field theory, as we have seen, explains many of the properties of compounds, but since it takes only the effect of ligands on the complexing agent into account, while the ligands themselves are regarded as invariable entities, the theory has significant limitations. It cannot, for example, be used to explain predominantly covalent and multiple bonds, and consequently to explain the structure and properties of many compounds.

1.4. Description of Complex Compounds by Molecular Orbital Theory

The most general and promising theory explaining the properties and structures of complexes is that of molecular orbitals, which allows for the structure of both the complexing agent and the ligands, as a single whole, or complex.

Octahedral complexes without π bonding. Let us consider the octahedral complexes of *d* elements. The system of coordinates for an octahedral complex with an ML_6 composition is as follows:



The valence orbitals of *d* elements are the *ns* and *np* orbitals of the outermost shell and the $(n - 1)$ *d* orbital of the penultimate one, close to it as regards energy. As we pointed out earlier, molecular orbitals are formed by the orbitals of interacting particles close in energy and spatial arrangement. Let us assume that only orbitals located on axes in the direction of the central atom (and therefore, for symmetry reasons, incapable of π bonding) are involved in the formation of bonds in ligands. In other words, let us consider octahedral complexes without π bonding.

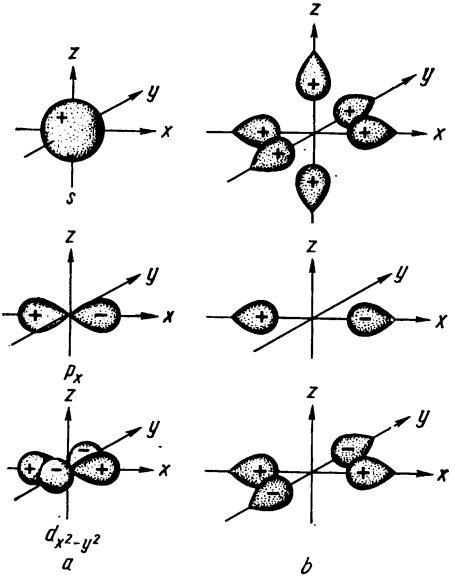


Fig. 212. Orbitals of the central atom and symmetrically corresponding combinations of ligand orbitals

Figure 212*a* and *b* shows possible combinations of the sigma-type valence orbitals of the central atom and symmetrically corresponding combinations of ligand orbitals. If we combine the pictures of the corresponding orbital of the central atom and the ligand orbitals, we will get a picture of their overlapping. As Fig. 212 shows, the *s* orbital of the complexing agent, because of spherical symmetry, is overlapped equally by the orbitals of each of the six ligands lying along the axes of the octahedron. Seven-centre bonding and antibonding (σ_s and σ_s^*) σ_s-molecular orbitals are thus formed.

Each of the three *p*-type orbitals can overlap the ligand orbitals located along the axes of the dumb-bell, which corresponds to the formation of three three-centre bonding and three antibonding σ_p orbitals (σ_x, σ_y, σ_z and σ_x^*, σ_y^*, σ_z^*).

Orbitals of $d_{x^2-y^2}$ and d_{z^2} type overlap ligand orbitals lying along the axes of their petals. Two bonding and two antibonding σ molecular orbitals ($\sigma_{x^2-y^2}$, σ_{z^2} and $\sigma_{x^2-y^2}^*$, $\sigma_{z^2}^*$) are formed as a result.

As for d_{xy}, d_{yz}, and d_{xz} orbitals, they are not combined with ligand orbitals (since their petals extend along the bisectors of the angles) (Fig. 213). In octahedral complexes without π bonding they act as one-centre nonbonding orbitals localised at the central atom. They are designated as π_d (π_{xy}, π_{yz}, π_{xz}).

The relative energy disposition of the molecular orbitals in the octahedral complexes of *d* elements is shown in Fig. 214.

Octahedral complexes have seven energy levels in the ground state, three bonding, three antibonding, and one nonbonding.

Depending on their degree of degeneracy, molecular energy levels are designated as *a* (for singly degenerate), *e* (for doubly degenerate)

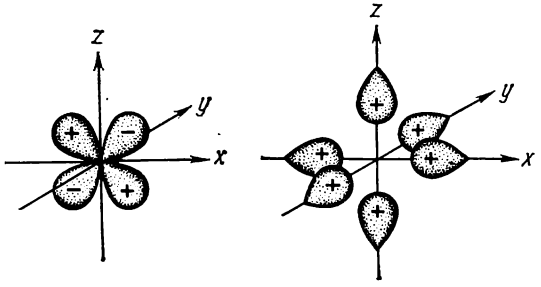


Fig. 213. Arrangement of the d_ε orbital of the central atom and combination of ligand orbitals

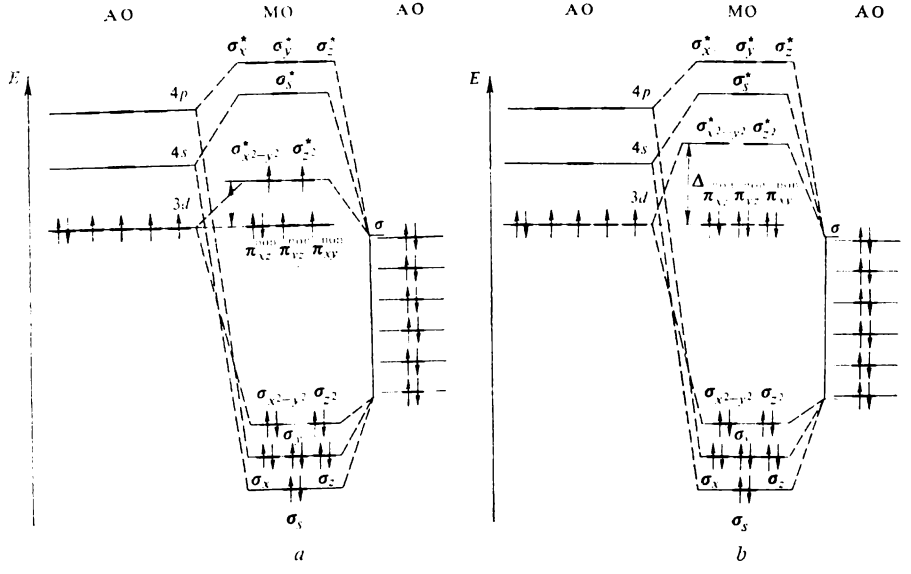


Fig. 214. Distribution of valence electrons in the molecular orbitals of (*a*) an octahedral high-spin complex $[CoF_6]^{3-}$ and (*b*) an octahedral low-spin complex $[Co(NH_3)_6]^{3+}$

and *t* (for triply degenerate levels). Molecular σ_s orbitals are designated accordingly as a_{1g} and a_{1g}^*; σ_d orbitals as e_g and e_g^*; σ_p orbitals as t_{1u} and t_{1u}^*; and π_d orbitals as t_{2g}. The *g*, 1*g*, 2*g*, and 1*u* designate the symmetry of the orbitals, while the asterisk, as usual,

designates an antibonding orbital. The letters *g* and *u* stand for the German *gerade* and *ungerade* (see p. 62).

Let us consider distribution of electrons in the molecular orbitals of a high-spin complex $[CoF_6]^{3-}$ (Fig. 214*a*) and a low-spin complex $[Co(NH_3)_6]^{3+}$ (Fig. 214*b*). It will be seen that 12 of the 18 valence

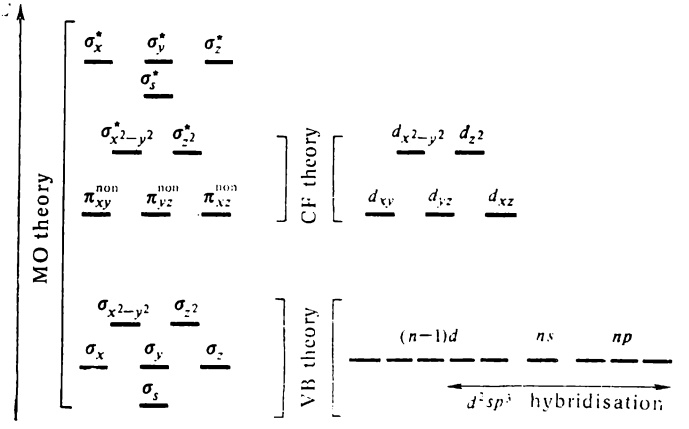


Fig. 215. A *d* element octahedral complex as interpreted by the theory of molecular orbitals (TMO), theory of valence bonds (VBT), and crystal field theory (CFT)

electrons of Co^{3+} (6 electrons) and the ligands (12 electrons), are in six bonding molecular σ orbitals, while the other six are distributed in $[CoF_6]^{3-}$ in nonbonding π_d^{non} and antibonding σ_d^* orbitals

$$[\sigma_s]^2\,[\sigma_p]^6\,[\sigma_d]^4\,[\pi_d^{non}]^4\,[\pi_d^*]^2$$

and in $[Co(NH_3)_6]^{3+}$ in nonbonding π_d^{non} orbitals only:

$$[\sigma_s]^2\,[\sigma_p]^6\,[\sigma_d]^4\,[\pi_d^{non}]^6$$

The difference in the character of electron distribution in π_d^{non} and σ_p^* orbitals depends on the value of Δ and is determined by the conditions discussed in the previous section.

Comparison of the molecular-orbital, valence-bond, and crystal field theories. The theory of molecular orbitals provides the most general approach for describing the properties of complex compounds, combining in itself the concepts of the valence bond and crystal field theories. The six σ orbitals of an octahedral complex in the valence bond theory correspond to the six σ bonds arising through a donor-acceptor interaction of the d^2sp^3 hybrid orbitals of the complexing agent and electron pairs of the six ligands (Fig. 215). As for the molecular π_d^{non} and σ_d^* orbitals, they correspond to *d* orbitals,

which arise, according to crystal field theory, through splitting of the d orbital in an octahedral ligand field (see Fig. 208).

The spectrochemical series of ligands. The order in which ligands are arranged in the spectrochemical series (see p. 508) can be explained by the MO theory as follows. The increasing degree of overlapping of the initial atomic orbitals corresponds to the increasing difference between the energies of the bonding and antibonding orbitals and the increasing value of Δ. In other words, Δ increases with

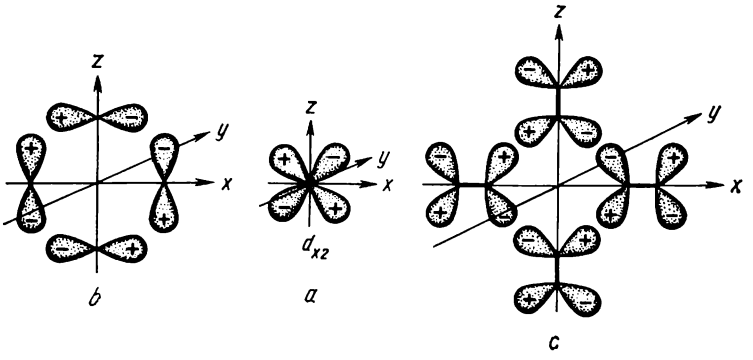


Fig. 216. (a) The d_g orbital of the central atom and the corresponding combinations (by symmetry) of (b) p and (c) π^* ligand orbitals, corresponding to the formation of molecular π orbitals of an octahedral complex

the strength of σ bonding in the metal-ligand system; its value also depends essentially on the π bonding between the central atom and ligands.

When the ligands have orbitals (vacant or occupied) which, because of symmetry, are capable of overlapping the d_{xy}, d_{yz} and d_{xz} orbitals of the central atom, the diagram of the molecular orbitals of a complex becomes much more complicated. Molecular orbitals of σ and σ^* type are then added to those of π and π^* type.

Ligand orbitals capable of π overlapping are, for example, the p and d atomic orbitals or molecular π and π^* orbitals of dinuclear molecules. Combinations of ligand orbitals and the d_{xz} orbital of the central atom, which, for symmetry considerations from molecular π orbitals, are shown in Fig. 216. The d_{xz} orbital and combination of molecular π or atomic d orbitals, and ligand orbitals of other types, may be combined in a similar way.

The involvement of d_{xy}, d_{yz}, and d_{xz} orbitals in the formation of π orbitals alters the value of Δ, which may increase or decrease depending on the ratio of the energy levels of the central atom's orbitals and those of the ligands combined with it. Figure 217a shows that

when ligand orbitals lying above the orbitals of the central atom are involved in the π interaction, the value of Δ rises, as happens with the overlapping of free *d* or π* orbitals of the ligands. During formation of π orbitals of the complex, some of the atom's electron density is displaced toward the ligands $M \xrightarrow{\pi} L$. This type of π interaction is known as *dative*.

When, however, ligand orbitals with energies lower than those of the d_{xy}, d_{yz}, and d_{xz} orbitals of the central atom are involved in

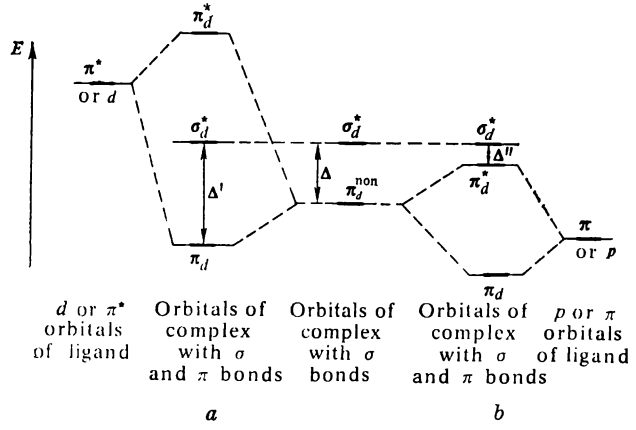


Fig. 217. Effect of the energy of π orbitals on the value of Δ

the π interaction, the value of Δ diminishes from the level characteristic of complexes with exclusively σ bonds (Fig. 217*b*). This is characteristic of the involvement of occupied *p* or π orbitals of ligands. During the formation of π* orbitals of a complex, some of the electron density is transferred from the ligands to the central atom $L \xrightarrow{\pi} M$. This type of π interaction is called *donor-acceptor*.

Thus, in addition to σ bonding, two types of π interaction are possible in complexes between the central atom and the ligands

π dative π donor-acceptor

M⊂L M⊂L

Donor Acceptor Acceptor Donor

Ligands that are pi acceptors have a higher Δ (i.e. cause significant splitting of the *d* orbital), while ligands that are pi donors, on the contrary, have a lower Δ (causing little splitting of the *d* level). All ligands can be divided into the following groups by the character

of the sigma and pi interaction:

σ Donors	NH_3, NR_3, NCS^-
σ Donors, weak π donors	F^-, OH^-, H_2O, ROH, R_2O
σ, π Donors, weak π acceptors	Cl^-, Br^-, I^-, SH^-, SCN^-
σ Donors, π acceptors	CN^-, CO, NO, PR_3, NO_2^-
π Donors, π acceptors	C_6H_6, C_2H_4

This table explains the order in which the ligands are arranged in the spectrochemical series

$$\underbrace{CO,\ CN^- > NO_2^-}_{\sigma\text{ donors, }\pi\text{ acceptors}} > \underbrace{NH_3 > NCS^-}_{\sigma\text{ donors}} > \underbrace{OH_2 > OH^- > F^-}_{\sigma,\pi\text{ donors}} > \underbrace{SCN^-,\ Cl^- > Br^- > I^-}_{\sigma,\pi\text{ donors, weak }\pi\text{ acceptors}}$$

Tetrahedral complexes with π bonding. Five $(n-1)d$, one ns, and three np orbitals of the central atom, and three p orbitals from each of the four ligands*, are involved in the formation of bonds in tetrahedral complexes and molecules of d elements of the MnO_4^-, CrO_4^{2-}, $TiCl_4$, and similar types.

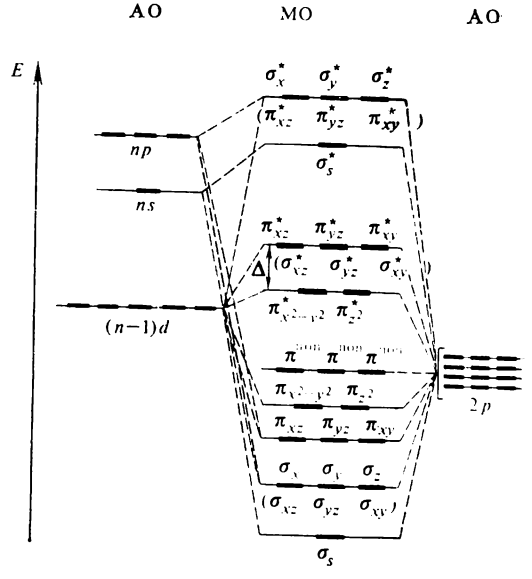


Fig. 218. The energy levels of a tetrahedral complex with π bonds

The 21 initial atomic orbitals of the central atom and four ligands form 21 molecular orbitals (Fig. 218).

Unlike the molecules and complexes of CH_4, NH_4^+, and BH_4^- type (see Fig. 45), σ orbitals of tetrahedral complexes and molecules of d elements are formed by the d_{xy}, d_{yz}, and d_{xz} orbitals of the central atom, as well as by the s and p or-

* The involvement of the s orbitals of the ligands can be disregarded for energy considerations.

bitals. Pi bonding, moreover, is very important in the tetrahedral complexes (molecules) of *d* elements, both the *p* and *d* orbitals of the complexing agent being involved in it.

Four of the 21 molecular orbitals of the tetrahedral complex act as σ orbitals and four as σ* orbitals; five are π, five π* orbitals, and three *p* orbitals belonging to the ligands act as nonbonding π^{non} orbitals.

Let us consider the distribution of electrons between the molecular orbitals of a tetrahedral complex, taking the MnO_4^- ion as an example. It contains 24 valence electrons (seven Mn electrons, four electrons from each oxygen atom, and one electron from the ion charge). This corresponds to the following electron configuration of the ion in the ground state: $(\sigma)^8\,(\pi)^{10}\,(\pi^{non})^6$.

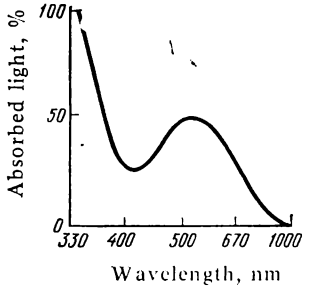


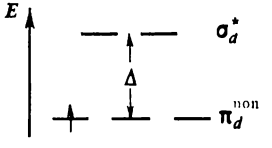
Fig. 219. The absorption spectrum of the $[Ti(OH_2)_6]^{3+}$ complex

According to the valence-bond theory, this distribution of electrons means that the MnO_4^- ion has four σ and five π bonds while the Mn atom is in an sp^3 (or d^3s) hybrid state stabilised by π bonding.

The valence electrons in the ions and molecules of the VO_4^{3-}, CrO_4^{2-}, TiO_4^{4-}, and $TiCl_4$ type, which are isoelectronic with the MnO_4^- ion, are distributed in the same way. The electrons in them are in bonding and nonbonding molecular orbitals only, which explains their stability.

Colour of complexes. Compounds of *d* elements are usually coloured, owing to the transition of electrons from a lower to a higher, unoccupied energy level through the absorption of quanta of visible light. The aqueous solution of Ti(III), for example, is violet. Its colour is due to the absorption spectrum of the complex $[Ti(OH_2)_6]^{3+}$ (Fig. 219). This octahedral complex has the electron configuration $(\sigma)^{12}(\pi_d^{non})^1(\sigma_d^*)^0$.

In order to excite an electron from the π_d^{non} to σ_d^* state, Δ energy has to be absorbed:



As Fig. 219 shows, this corresponds to the absorption of a wavelength of 500 nm. Thus, the solutions of $[Ti(OH_2)_6]^{3+}$ absorb yellow rays and transmit blue and red radiation, which accounts for their violet colour.

Study of the absorption spectra of compounds makes it possible to determine Δ:

$$\Delta = h\nu = hc/\lambda$$

For the $[Ti(OH_2)_6]^{3+}$ ion Δ is 238 kJ/mol.

The absorption spectra of complexes containing more than one π electron are more complicated since a greater number of electron transitions is possible. The discussed type of transition considered is known as a d—d transition.

The colour of complexes may also be due to what are called electron transitions with *charge transfer*. The colour of the ions MnO_4^- (violet) and CrO_4^{2-} (yellow), for example, can be explained by the transition of nonbonding π^{non} electrons (localised at the oxygen atoms) to antibonding π_d^* orbitals (predominantly localised at the central Mn or Cr atom respectively).

1.5. Electron Configuration of Complexing Agents and Structure of Complexes

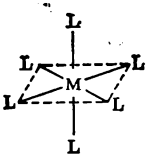
The spatial configuration adopted by a complex depends essentially on the way its electrons are distributed in the molecular orbitals and on the value of Δ. The electron density of octahedral complexes, for instance, is most symmetrical with the following configurations:

Complexes	Central ion (atom)
$[\sigma]^{12}[\pi]_d^{non}]^3$	d^3—Cr(III), Mn(IV)
$[\sigma]^{12}[\pi_d^{non}]^3[\sigma_d^*]^2$	d^5—Mn(II), Fe(III)
$[\sigma]^{12}[\pi_d^{non}]^6]\sigma_d^*]^2$	d^8—Ni(II)
$[\sigma]^{12}[\pi_d^{non}]^6$	d^6—Co(III), Fe(II), Pt(IV), Pd(IV)

Octahedral complexes are consequently most characteristic of central ions with a d^3, d^5, or d^8 configuration and, when the value of Δ is high, with a d^6 configuration.

With other electron configurations there is varying distortion of the octahedral structure. The distribution of electrons in molecular orbitals is not symmetrical, for instance, with a d^4—Cr(II), Mn(III) or d^9—Cu(II) configurations of the central ion (atom): $[\sigma]^{12}[\pi_d^{non}]^3[\sigma_d^*]^1$ and $[\sigma]^{12}[\pi_d^{non}]^6[\sigma_d^*]^3$.

The presence of one (d^1) or three (d^9) electrons in the antibonding molecular σ_d^* orbitals corresponds to a weakening of two (of the six) σ metal—ligand bonds. Four of the six ligands L located at the angles of the square are, therefore, closer to the central ion than the other two, which are above and below it:

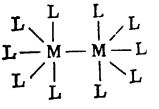


If the value of Δ is high, this distortion may be quite significant, and the octahedron will be converted into a planar square, as happens in several complexes with $Cu^{2+}(d^9)$, e.g. $Cu(CN)_4^{2-}$.

An octahedral structure is also not advantageous for a d^8 configuration with a high value of Δ, since two electrons are in the strongly antibonding molecular σ_d^* orbitals. Complexes in the form of a planar square such as those produced by Pt^{2+}, Pd^{2+}, and Au^{3+} (d^8) (the *d* elements of the 5th and 6th periods) with a high value of Δ are typical of such cases.

Since CN^- ions generate a strong field (Δ is high), the $Ni(CN)_4^{2-}$ ion (the configuration of Ni^{2+} being d^8) also has a square structure.

With high values of Δ, octahedral complexes are not suitable for atoms and ions with a d^7 configuration, since there is one electron in a strongly antibonding molecular σ_d^* orbital. Dimer complexes with σ metal—metal bonds are then more typical (for example with strong CN^- or CO ligand fields):



In high-spin octahedral complexes with d^1 and d^6, d^2 and d^7 configurations of the central ion, the distortion is insignificant and cannot be determined experimentally.

The size of the ligands, which, naturally, are mutually repelled, also affects the character of a structure. Thus, Mn^{2+} and Fe^{3+} (d^5) produce octahedral complexes with F^- ions (MnF_6^{4-} and FeF_6^{3-}) but tetrahedral complexes with larger ions of Cl^- ($MnCl_4^{2-}$ and $FeCl_4^-$).

Other factors affecting the structure of complexes will be discussed in the appropriate contexts below.

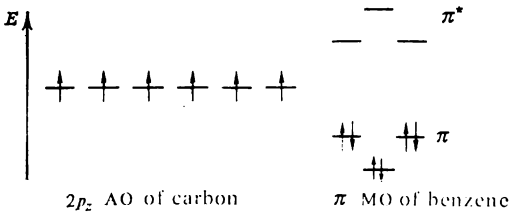
1.6. Complexes with Organic Unsaturated Molecules and Ions as Ligands

Complexes with molecules of organic compounds with π bonds (C_6H_6, C_2H_4, C_2H_2, etc.) are very characteristic of the chemistry of *d* elements.

Complexes with cyclic unsaturated molecules. Let us consider derivatives of *d* elements of the type of $Cr(C_6H_6)_2$ and $Fe(C_5H_5)_2$. Dark brown *dibenzene chromium* $Cr(C_6H_6)_2$ (m.p. 284 °C) and orange-brown *ferrocene* $Fe(C_5H_5)_2$ (m.p. 173 °C) are stable, crystalline, diamagnetic solids.

X ray crystallography indicates that the metal atom is at the middle of such compounds, with the organic cyclic molecules lying on both sides of it in parallel planes (see Fig. 220), a structure known as a *molecular sandwich*. Such structures are formed because of the capacity of ligands of C_6H_6 and $C_5H_5^+$ type for π dative and π donor-acceptor interactions with the atoms (ions) of *d* elements through (symmetrically) suitable filled and unoccupied π antibonding molecular orbitals. As was pointed out earlier (p. 87), the $2p_z$ electrons of the six car-

bon atoms form a nonlocalized π bond in a benzene molecule. According to the MO theory, this corresponds to the formation of six π molecular orbitals, three of which are bonding and the others antibonding, of six $2p_z$ atomic orbitals:



The six $2p_z$ electrons of the six carbon atoms occupy three bonding orbitals, while three π orbitals remain unoccupied.

The chemical bond in $Cr(C_6H_6)_2$ is formed by the π donor-acceptor and dative mechanisms by 18 electrons (six from the chromium atom and 12 π electrons

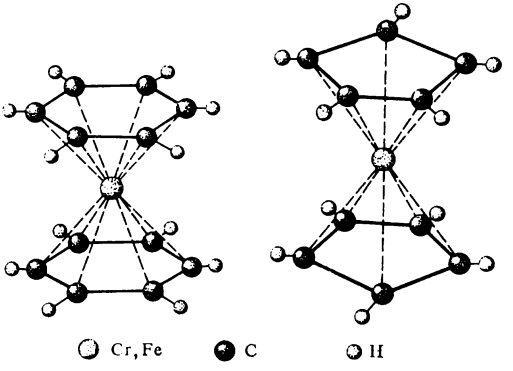
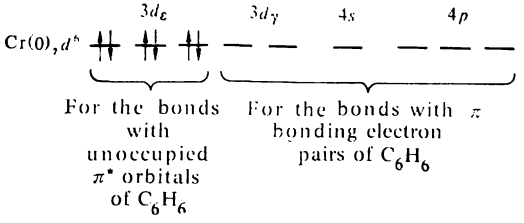


Fig. 220. Structure of chromium dibenzene $Cr(C_6H_6)_2$ and ferrocene $Fe(C_5H_5)_2$

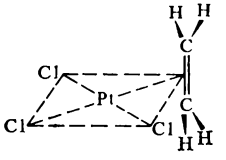
of two C_6H_6 molecules) and unoccupied *d* orbitals of the chromium atom and π^* orbitals of two benzene molecules:



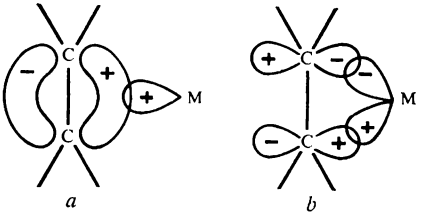
A system of 18 electrons thus arises, distributed in nine multicentre molecular orbitals and moving in a field of 13 nuclei (one Cr atom and 12 C atoms of two benzene rings).

In a molecule of ferrocene $Fe(C_5H_5)_2$, 18 electrons (eight from the Fe atom and ten π electrons of two C_5H_5 radicals) are present in a field of 11 centres (one Fe atom and ten C atoms of two C_5H_5 rings).

Complexes with ethylene and acetylene. Compounds with C_2H_4 and C_2H_2 as ligands are quite varied. A pale yellow salt with a $K[PtCl_3(C_2H_4)]$ composition has been isolated, in which the C_2H_4 molecule is one of the ligands in the complex ion. The structure of the ion $[PtCl_3(C_2H_4)]^-$ can be represented by the following diagram:



The ability of the C_2H_4 ($H_2C=CH_2$) molecule to act as a ligand is due to its ability to be a π acceptor and π donor. The bond between the metal atom and the C_2H_4 molecule is formed as follows:



In (*a*) the donor-acceptor bond ($C_2H_4 \rightarrow M$) is formed by a π electron pair of the C_2H_4 molecule and an unoccupied *d* orbital of the metal atom; in (*b*) a dative bond ($M \rightarrow C_2H_4$) is formed by a *d* electron pair of the metal atom and a free π^* orbital of the C_2H_4 molecule.

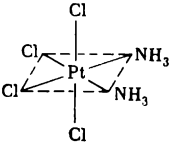
The complexes of *d* elements with acetylene have a similar structure.

1.7. Isomerism of Complex Compounds

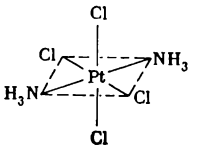
As will be recalled, isomerism is a very common phenomenon in the chemistry of complex compounds, in which substances of the same composition have a different structure and hence different properties, and is one of the causes of the variety of complex compounds. Geometrical, coordination, ionisation, and other types of isomerism are distinguished.

Geometrical (*cis-trans*) *isomerism* occurs in complexes with heterogeneous ligands, e.g. $[Pt(NH_3)_2Cl_4]$ and $[Pt(NH_3)_2Cl_2]$. The first of these complexes (platinum diamminotetrachloride) exists in two

forms with an octahedral structure



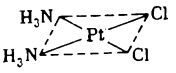
cis-Isomer (orange)



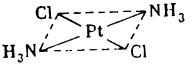
trans-Isomer (yellow)

In one form, the ammonia molecules are located at neighbouring apexes of the octahedron, and the compounds are known as *cis-isomers* (Latin *cis* on this side). In the other form, the ammonia molecules are positioned at opposite apexes. Compounds of this type are called *trans-isomers* (Latin *trans* across, over).

Platinum diamminodichloride $[Pt(NH_3)_2Cl_2]$, a square complex, can also exist as *cis-* and *trans*-isomers:



cis-Isomer (orange-yellow)



trans-Isomer (pale yellow)

The study of geometrical isomerism was important in the establishing of the spatial configuration of complexes. Werner, for instance, studied complexes of an MA_4B_2 and MA_2B_2 composition. In six coordinate complexes, an octahedral model presumes the existence of two geometrical isomers, while models of a hexagon and a trigonal prism allow for the existence of three isomers. Since it had not proved possible to synthesise more than two isomers of MA_4B_2 complexes, Werner concluded that complexes with a coordination number of six must have an octahedral structure.

Complexes with a coordination number of four (MA_2B_2) may have a square or tetrahedral structure. Square complexes can have two geometrical isomers, but such isomers are impossible with a tetrahedral structure. Isomers of compounds with a coordination number of four for the complexing agent can thus have a square structure only. Werner's hypothesis was later proved experimentally and theoretically on the basis of quantum-mechanical conceptions.

Coordination isomerism is due to a different coordination of ligands of *two* types with respect to *two* different complexing agents: e.g.

$$[Co(NH_3)_6][Cr(CN)_6] \quad [Cr(NH_3)_6][Co(CN)_6]$$

Ionisation isomerism is displayed in uneven distribution of anions between the inner and the outer spheres, for example, in compounds

with the following composition:

$$\underset{\text{Red-violet}}{[CoBr(NH_3)_5]SO_4} \qquad \underset{\text{Red}}{[CoSO_4(NH_3)_5]Br}$$

The bromide ion cannot be precipitated from a solution of the reddish-violet isomer, but $BaSO_4$ can be precipitated by the Ba^{2+} ion. On the contrary, the SO_4^{2-} ion cannot be precipitated from a solution of the red isomer, while silver nitrate precipitates silver bromide.

Other types of isomerism are also known (see, for example, p. 559).

CHAPTER 2

Group III *d* Elements

The *d* elements of Group III of the periodic system (scandium Sc, yttrium Y, lanthanum La and actinium Ac) are full electron analogues and form the scandium subgroup. Their main constants (and those of boron and aluminium) are as follows:

	$_5$B	$_{13}$Al	$_{21}$Sc	$_{39}$Y	$_{57}$La	$_{89}$Ac
Atomic mass	10.811	26.8815	44.956	88.905	138.91	227
Valence electrons	$2s^22p^1$	$3s^23p^1$	$3d^14s^2$	$4d^15s^2$	$5d^16s^2$	$6d^17s^2$
Metal atom radius, nm	0.091	0.143	0.164	0.181	0.187	0.203
Conventional ion E^{3+} radius, nm	0.020	0.057	0.083	0.097	0.104	0.111
Ionisation energy $E \rightarrow E^+$, eV	8.298	5.986	6.56	6.22	5.58	5.1
Abundance, mole per cent	6×10^{-4}	6.6	3×10^{-4}	2.6×10^{-4}	2.5×10^{-4}	5×10^{-15}
Stable isotopes	^{10}B (19.61%) ^{11}B (80.39%)	^{27}Al (100%)	^{45}Sc (100%)	^{89}Y (100%)	^{139}La (99.91%) ^{139}La (0.089%)	none

Scandium and its analogues are the first *d* elements of their periods, i.e. are the first whose *d* orbitals of the penultimate shell begin to be filled. The presence of just one electron in the *d* state accounts for the low stability of the d^1s^2 configuration and affects all properties of the elements in this subgroup. In particular, scandium and its analogues, in contrast to the other *d* elements, have a stable +3 oxidation state. Their coordination numbers, on the contrary, are unstable. In the transition from scandium to yttrium and lanthanum the stable coordination numbers increase. A coordination number of six is typical of scandium(III); for Y and La it rises to eight and nine.

This marked tendency to high coordination numbers is a main feature of the stereochemistry of *d* elements of the beginning of

the fifth and sixth periods, distinguishing it from that of those of the beginning of the fourth period. The typical coordination numbers, corresponding to the highest oxidation state of the first five *d* elements are as follows:

Sc(III)	Ti(IV)	V(V)	Cr(VI)	Mn(VII)
6	6, 4	6, 4	4	4
Y(III)	Zr(IV)	Nb(V)	Mo(VI)	Tc(VII)
8, 9	6, 7, 8	6, 7, 8	6, 4	4, 6
La(III)	Hf (1V)	Ta(V)	W(VI)	Re(VII)
8, 9	6, 7, 8	6, 7, 8	6, 4	4, 6

As the number of valence electrons diminishes, and the number of free valence orbitals increases, i.e. with displacement to the left in the periodic table, there is a greater tendency toward higher stable coordination numbers.

Comparison of the electron structures of the atoms and ions of scandium, gallium, and aluminium indicates that the first two have nothing in common with aluminium as regards the structure of the outermost electron shell of their atoms in the ground state, while the electron structure of their tripositive ions is the same:

	Atom	Ion E^{3+}
Al	2, 8, 3	2, 8
Sc	2, 9, 2	2, 8
Ga	2, 18, 3	2, 18

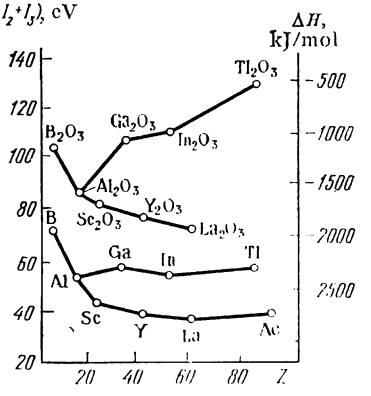


Fig. 221. The sum of three first ionisation energies of atoms and enthalpies of formation of the E_2O_3 oxides of Group III elements

The elements of the gallium subgroup, on the contrary, have an atomic structure similar to aluminium in the ground state, but much different structures of their E^{3+} ions.

Furthermore, in the B—Al—Sc—Y—La—Ac series (in contrast to the B—Al—Ga—In—Tl series) atomic and ionic radii increase uniformly (see Fig. 17). Thus, it is to be expected that the properties of similar compounds in the B—Ac series will also change uniformly, in contrast to the B—Tl series. This is confirmed, for example, when we compare the sum of three first ionisation energies of the atoms and the enthalpies of formation of compounds of the scandium and gallium subgroups and of the typical Group III elements (Fig. 221). As will be seen from the figure, the energies of three-fold ionisation $(I_1 + I_2 + I_3)$ decrease uniformly and while the enthalpies of formation of the highest oxides increase throughout the B—Ac series

(*p* and *d* elements), there is no such uniformity in the B—Tl series (of *p* elements only). The pattern considered is another illustration of secondary periodicity (see Fig. 18).

Metallic properties strengthen regularly in the B—Al—Sc—Y—La—Ac series. Scandium resembles aluminium and is an amphoteric element; its analogues are close in properties to the alkaline earth metals.

2.1. Scandium Subgroup

The elements of the scandium subgroup are very dispersed in the Earth's crust and do not form separate minerals. For that reason they are difficult to isolate in the pure state (without admixtures).

The simple substances. The elements of the scandium subgroup are white metals as simple substances. Some of their constants are as follows:

	Sc	Y	La	Ac
Density, g/cm³	3.0	4.47	6.16	10.1
M. p., °C	1539	1525	920	1040
B. p., °C	2700	3025	3370	—
E°_{298}, V	—2.08	—2.37	—2.52	—2.6

The simple substances are very reactive, second only to the alkali and alkaline earth metals. Their activity rises markedly in the Sc—Y—La—Ac series as is shown, for example, by their electrode potentials E°_{298}. When heated (more or less strongly) all react with most nonmetals, and with metals as well, when fused.

Scandium and its analogues precede hydrogen in the electromotive series (see their E°_{298} values). Scandium does not react with water, in which it is passivated, while lanthanum decomposes water in normal conditions:

$$2La + 6H_2O = 2La(OH)_3 + 3H_2$$

The metals readily react with dilute acids, dilute HNO_3 being reduced to NH_4NO_3:

$$8\overset{0}{Sc} + 30H\overset{+5}{N}O_3 = 8\overset{+3}{Sc}(NO_3)_3 + 3\overset{-3}{N}H_4NO_3 + 9H_2O$$

Scandium and its analogues form high-melting compounds of an intermetallic type, for example, ScB_2, YB_2, LaB_6, ESi_2, YC_2, LaC_2, ScC, etc.

In the free state Sc, Y, and La are obtained by electrolysis of molten chlorides or by a metallothermic process.

2.2. Compounds of the Scandium Subgroup Elements

As metallic character strengthens in the Sc—Y—La—Ac series, acidic properties weaken in the E(III) compounds and basic features increase. E(III) compounds are mostly white crystalline solids.

The structure of these compounds have high coordination numbers of E. The coordination number of La(III), for example, is nine in crystalline $LaCl_3$ and $La(OH)_3$, and eight in crystals of La_2S_3 and LaN.

The nitrates, sulphates, and halides (except EF_3) are soluble in water, the hydroxides, carbonates, phosphates, fluorides, fluosilicates, etc., are barely soluble. (As with Group II *s* elements, the solubility of the sulphates decreases rapidly in the Sc—Y—La series.) Crystal hydrates with a varying number of water molecules are precipitated from aqueous solutions, e.g. $Sc_2(SO_4)_3 \cdot 5H_2O$, $Y_2(SO_4)_3 \cdot 7H_2O$, $EHal_3 \cdot 6H_2O$, $Y_2(CO_3)_3 \cdot 3H_2O$, $La_2(SO_4)_3 \cdot 8H_2O$.

The E_2O_3 *oxides* are high-melting white crystals with high enthalpies of formation (ΔH_f° from —1650 to—2000 kJ/mol). The interaction of La_2O_3 and water is accompanied with liberation of heat (slaking):

$$La_2O_3 + 3H_2O = 2La(OH)_3, \quad \Delta H < 0$$

The activity of the interaction with water increases in the Sc_2O_3—Y_2O_3—La_2O_3—Ac_2O_3 series.

Basic properties strengthen, and solubility increases, in the *hydroxide* series [$Sc(OH)_3$—$Y(OH)_3$—$La(OH)_3$—$Ac(OH)_3$]. Thus, $Sc(OH)_3$ is amphoteric, while $La(OH)_3$ is quite a strong base that reacts only with acids in normal conditions, absorbs carbon dioxide, and displaces ammonia from its compounds when heated. When Sc_2O_3 or $Sc(OH)_3$ are heated with basic oxides or alkalis, oxyscandiates of $\overset{+1}{M}ScO_2$ type are formed, while hydroxyscandiates are formed in solutions, e.g.

$$3NaOH + Sc(OH)_3 = Na_3[Sc(OH)_6]$$

Basic properties also increase in the *halide* series [$ScHal_3$—$YHal_3$—$LaHal_3$—$AcHal_3$], so that only ScF_3 tends to form complex halides in solutions for which fluoroscandiates $\overset{+1}{M}_3[ScF_6]$ are known. The fluoroscandiates of Group I *s* elements are soluble in water and are quite stable. Fluoroyttriates, however, are obtained only by fusing YF_3 with fluorides of the most typical metallic elements, such as caesium, rubidium, and potassium ($Cs_3[YF_6]$, $Rb_3[YF_6]$). The only fluorolanthanate known is the caesium derivative $Cs_3[LaF_6]$. Complex derivatives of the other halides are even less stable.

The fluorides of Sc(III) and its analogues, like those of aluminium(III), differ substantially from the other halides. They are high-melting (m.p. 1450 °C to 1550 °C), nonhygroscopic compounds, insoluble in water. The chlorides, bromides, and iodides (m.p. 800 °C to 900 °C), on the contrary, are hygroscopic, soluble in water, and readily hydrolysed, forming polymeric EOHal oxyhalides.

Like aluminium, scandium and its analogues form double salts, for example, $\overset{+1}{M}[E(SO_4)_2]$, $\overset{+1}{M}_2[E(NO_3)_2]$, $\overset{+1}{M}[E(CO_3)_2]$, which explains the solubility of their carbonates in saturated solutions of the carbonates of alkali metals and NH_4^+:

$$K_2CO_3 + La_2(CO_3)_2 = 2K[La(CO_3)_2]$$

Compounds of scandium subgroup are used in semiconductor industry.

From the foregoing it follows that scandium and its analogues resemble *s* elements in their properties, i.e. are transitional between the *d* and *s* elements of the long periods.

CHAPTER 3

Group IV *d* Elements

The *d* elements of Group IV—titanium Ti, zirconium Zr, hafnium Hf, and kurchatovium Ku—are full electron analogues, and form a titanium subgroup.

	$_{22}$Ti	$_{40}$Zr	$_{72}$Hf	$_{104}$Ku
Atomic mass	47.90	91.22	178.49	[260]
Valence electrons	$3d^24s^2$	$4d^25s^2$	$5d^26s^2$	$6d^27s^2$*
Metal atom radius, nm	0.146	0.160	0.159	0.16*
Conventional ion E^{4+} radius, nm	0.064	0.082	0.082	0.078*
Ionisation energy $E^0 \rightarrow E^+$, eV	6.82	6.84	7.5	—
Abundance, mole per cent	0.25	4×10^{-3}	5×10^{-5}	—

* Predicted.

As will be seen from this table, the first ionisation energies rise a bit in the Ti—Zr—Hf series. The atomic and ionic radii also increase in the transition from Ti to Zr, while the atoms and ions of zirconium and hafnium, because of lanthanide contraction, are almost equal in size. The properties of Zr and Hf are therefore very similar, so that it is very difficult to separate them.

In contrast to elements of the germanium subgroup, the stable oxidation state rises in the titanium subgroup with atomic number. The stablest oxidation state of titanium and its analogues is +4 though numerous compounds of Ti(III) and a few of Ti(II) are also known. Thus, the oxides TiO, TiO_2, and Ti_2O_3, and the fluorides TiF_2, TiF_3, and TiF_4 are stable compounds of titanium, and ZrO_2 and HfO_2, and ZrF_4 and HfF_4 are stable oxides and fluorides of zirconium and hafnium. Taking the fluorides as an example, this empirical fact can be explained as follows. The formation of compounds from the simple substances requires energy to break the bonds in them and is accompanied with a liberation of energy during the interaction of the atoms formed. The bond energy of metals (heat of atomisation) is much higher than the bond energy of nonmetals (F_2). During the formation of EF_2, EF_3, and EF_4, the expenditure of energy on atom-

isation of the metals is the same, but the gain in energy during the union of the E and F atoms is smaller in the formation of EF_2 than of EF_3 and EF_4. Consequently, if the heat of atomisation of a metal is high enough, it is more energy advantageous when higher rather than lower fluorides are formed. Since the heat of atomisation (sublimation) increases with atomic number in the subgroups of *d* elements, the formation of fluorides with the highest oxidation states of the element becomes more advantageous.

A coordination number of six is typical of titanium, four being less typical; coordination numbers seven and eight are more characteristic of zirconium and hafnium.

Table 46. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of Elements of the Titanium Subgroup**

Oxidation state	Electron configuration	Coordination number	Spatial configuration of complex	Typical compounds
+2	d^2	6	Octahedron	TiO, TiF_2, $TiCl_2$
+3	d^1	6	Octahedron	$[Ti(OH_2)_6]^{3+}$, $[TiF_6]^{3-}$, Ti_2O_3, $TiCl_3$
+4	d^0	4	Tetrahedron	$TiCl_4$, $ZrCl_4$ (g), Ba_2TiO_4
		6	Octahedron	TiF_6^{2-}, TiO_2, $CaTiO_3$ (perovskite), $FeTiO_3$ (ilmenite)
		7	See Fig. 226	ZrF_7^{3-}, ZrO_2, HfO_2
		8	Square antiprism	$[Zr_4(OH)_8(OH_2)_{16}]^{8+}$, ZrF_8^{4-}, ZrO_2 (CaF_2 type)

3.1. Titanium Subgroup

Natural titanium and zirconium each have five isotopes, and hafnium six. Kurchatovium has been synthesised in the laboratory. Titanium is quite abundant in the Earth's crust, occurring mainly as the minerals *rutile* TiO_2, *ilmenite* $FeTiO_3$, and *perovskite* $CaTiO_3$. Zirconium and hafnium are dispersed elements; the most important zirconium minerals are *zircon* $ZrSiO_4$ and *baddeleyite* ZrO_2. Hafnium does not form independent minerals and always occurs with zirconium.

The simple substances. As simple substances, titanium, zirconium and hafnium are silvery-white metals. Titanium is a light metal and zirconium and hafnium heavy ones. All are high-melting. In normal conditions their α modification (hexagonal lattice) is stable and at

high temperatures the β modification (body-centred cubic lattice). Their basic constants are as follows:

	Ti	Zr	Hf	Ku
Density, g/cm³	4.50	6.45	13.1	18*
M. p., °C	1667	1852	2220	2100*
B. p., °C	~ 3330	~ 4380	~ 5000	5500*
S°_{298}, J/K·mol	30.6	39.0	43.6	—
Electrical conductivity	1	2	3	—
$\Delta H^\circ_{\text{subl.,}\ 298}$, kJ/mol	471	608	703	—

* Predicted.

The pure metals are easy to work mechanically. Admixtures of O, N, C, and H, it should be noted, alter the plasticity, malleability, ductility, tensile strength, hardness, and other mechanical properties of the metals.

At normal temperatures they are corrosion-resistant in air, owing to the presence of a protective film of oxide EO_2 on their surface. When heated their activity increases noticeably; when red hot they burn in oxygen to form EO_2. At 800 °C they react actively with nitrogen, forming EN. Between 150 °C and 400 °C, they react with the halogens to form $EHal_4$, etc. The metals are pyrophoric in the powdered state.

Titanium, zirconium, and hafnium are chemically stable in many aggressive media; titanium, for instance, resists the action of solutions of sulphates, chlorides, sea water, etc. The metals are passivated in nitric acid. Titanium, when heated, unlike zirconium and hafnium, is soluble in hydrochloric acid, forming aquo complexes of Ti(III), $[Ti(OH_2)_6]^{3+}$, in a reducing atmosphere of H_2:

$$2\overset{0}{Ti} + 6H_3^+ + 6H_2O \quad 2[\overset{+3}{Ti}(OH_2)_6]^{3+} + 3H_2$$
$$Ti^{3+} + 3e^- = Ti, \quad E^\circ_{298} = -1.23\ V$$

Zirconium and hafnium react with acids only when conditions are created for oxidation and the formation of E(IV) anion complexes; finely ground Zr and Hf, like Ti, dissolve comparatively readily in hydrofluoric acid

$$\overset{0}{E} + 6HF = H_2[\overset{+4}{E}F_6] + 2H_2$$
$$TiF_6^{2-} + 4e^- = Ti + 6F^-, \quad E^\circ_{298} = -1.19\ V$$

in a mixture of acids $HF + HNO_3$, in concentrated H_2SO_4, and in aqua regia:

$$3\overset{0}{E} + 4HNO_3 + 18HF = 3H_2[\overset{+4}{E}F_6] + 4NO + 8H_2O$$
$$\overset{0}{Zr} + 5H_2SO_4 = H_2[\overset{+4}{Zr}(SO_4)_3] + 2SO_2 + 4H_2O$$
$$3\overset{0}{Zr} + 4HNO_3 + 18HCl = 3H_2[\overset{+4}{Zr}Cl_6] + 4NO + 8H_2O$$

Titanium is less stable than zirconium and hafnium in alkali solutions.

Since Ti, Zr, and Hf are chemically very reactive at high temperatures, it is difficult to isolate them in the pure state, and they are obtained, as a rule, by magnesiothermic or sodiothermic reduction of their tetrahalides in an atmosphere of argon or helium

$$TiCl_4 + 2Mg = 2MgCl_2 + Ti$$
$$K_2[ZrF_6] + 4Na = 4NaF + 2KF + Zr$$

Very pure metals are obtained by thermal decomposition of the tetraiodides EI_4 (at high temperatures in vacuum). Figure 222 illustrates a Pyrex vessel used for obtaining pure titanium. Powdered titanium and iodine are put into it through an inlet tube *1*, and air is evacuated through a tube *2*. The vessel is heated in an electric furnace to 600 °C, while a titanium wire *3* is heated by electric current. At 200 °C the titanium reacts with the iodine to form TiI_4 which sublimes at 377 °C. The TiI_4 vapour is decomposed on contact with the titanium wire heated to between 1100 °C and 1400 °C and pure metallic titanium deposits on the wire, while the iodine vapour is condensed on the cold parts of the apparatus. Titanium of very high purity can be obtained in this way, since most of the impurities in the initial powder either do not react with iodine or do not form volatile iodides (at 377° C). The titanium metal so obtained is in the form of rods 5 to 30 mm long.

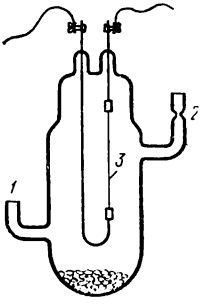


Fig. 222. Vessel for obtaining titanium by thermal decomposition of TiI_4

The titanium and zirconium employed in the steel industry are produced as *ferrotitanium* and *ferrozirconium* (15 to 50 per cent Ti or Zr) by joint reduction of titanium or zirconium minerals and iron ores by coal.

Because of its high thermal stability and corrosion resistance, titanium is an important engineering material, and is employed in the building of aircraft, submarines, etc. Zirconium (freed of hafnium), and certain of its alloys, are employed in nuclear power engineering as materials that reflect neutrons. The field of application of hafnium is more limited. It is also employed in nuclear power engineering, but solely as an absorber of neutrons. It is also used in electronics (as cathodes of television tubes).

3.2. Compounds of the Titanium Subgroup Elements

Metallic and metal-like compounds. Powdered titanium, zirconium, and hafnium absorb hydrogen, oxygen, and nitrogen. The dissolved nonmetals are converted to the atomic state and become

involved in the formation of chemical bonds. In addition to the strongly delocalised (metallic) bonds, localised (covalent) ones are also formed, so that the metals become much harder and brittler. The ability of titanium, zirconium, and hafnium to absorb gases is utilised to obtain a high vacuum, and to extract gases from alloys, etc.

The *hydrides* of titanium, zirconium and hafnium, are brittle, metal-like, black or grey powders. Their idealised composition corresponds to the formula EH_2. These compounds are intermediate between solid solutions and salt-like (ionic) hydrides of the CaH_2 type.

The decomposition of titanium, zirconium, and hafnium hydrides is used to obtain the metals in powdered form and to coat the surfaces of various articles, with them.

The sequence of the stages in the oxidation of titanium by oxygen can be expressed as follows:

$$Ti + O_2 \rightarrow \underset{\text{Solid solution}}{Ti-O} \rightarrow Ti_6O \rightarrow Ti_3O \rightarrow TiO \rightarrow Ti_2O_3 \rightarrow TiO_2$$

As the oxygen content increases, the proportion of metallic bonds decreases and of covalent bond increases. Ti_6O and Ti_3O are typical metallic compounds, while TiO_2 is predominantly a covalent compound ($\Delta E = 3.06$ eV).

The *carbides* and *nitrides* of the titanium subgroup are formed by direct interaction of the simple substances at high temperatures. The EN and EC compounds (of various composition) are crystalline solids, very hard, refractory (3000 °C to 4000 °C), good conductors of electricity, and chemically inert. The *silicides* ESi_2, and the *borides* EB and EB_2, have the same properties. They all, of course, have a variable composition. The compounds TiC, TiN, TiO, ZrN, ZrC, and HfC have a structure of NaCl type and form solid solutions with one another.

The valuable physicochemical properties of the metalloids of the titanium subgroup make them highly valuable in engineering. The alloy containing 20 per cent HfC and 80 per cent TiC, for example, is one of the most refractory materials known (m.p. 4400°C).

The character of the interaction of titanium and its analogues with metals depends on the position of the latter in the periodic table. Chromium and vanadium, for instance, which are close to titanium in their properties, form a continuous series of substitutional solid solutions with it:

	Ti	V	Cr	Mn	Fe	Co	Ni
Valence electrons	d^2s^2	d^3s^2	d^5s^1	d^5s^2	d^6s^2	d^7s^2	d^8s^2
Solubility in Ti, mole per cent	—	100	100	28	20	13	10

The possibility of forming solid solutions with titanium falls in the Mn—Fe—Co—Ni series, but the tendency to form intermetallic compounds increases. Thus, titanium reacts quite energetically in the molten state with iron to form Fe_3Ti and FeTi. So, too, do Co, Ni, Cu, and Zn, which form compounds of the M_3Ti and MTi type with titanium.

The addition of titanium and zirconium to alloys gives them valuable physicochemical properties. Thus, the addition of even 0.1 per cent of titanium to steel lends it hardness and elasticity; such steels are employed to make rails, railway wheels and axles, etc. Steels with an admixture of zirconium have increased hardness and toughness, and are used to make armour plate.

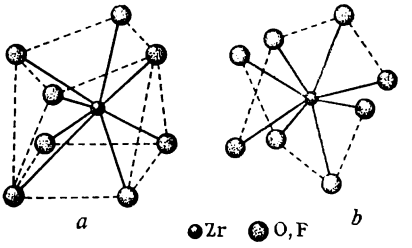


Fig. 223. The arrangement of atoms in the octahedra of (*a*) ZrO_8 and (*b*) ZrF_8

Compounds of Ti(IV), Zr(IV) and Hf(IV). Dioxides EO_2, tetrahalides $EHal_4$, disulphides ES_2, disulphates $E(SO_4)_2$, etc., are known for titanium and its analogues. Numerous titanates, zirconates and hafnates, derivatives of E(IV) anion complexes, are also known:

$EHal_4$	EO_2	ES_2	$E(SO_4)_2$
$[EHal_6]^{2-}$	EO_4^{4-}	ES_4^{4-}	$[E(SO_4)_3]^{2-}$
$[ZrF_7]^{3-}$, $[HfF_7]^{3-}$	EO_3^{2-}	ES_3^{2-}	
$[ZrF_8]^{4-}$, $[HfF_8]^{4-}$			

A coordination number of six, and less often of four are most characteristic of titanium(IV). Zirconium(IV) and hafnium(IV) have also coordination numbers of seven and eight in their compounds (see Table 46).

The EO_2 *dioxides* have coordination crystal lattices. One form of TiO_2, *rutile*, has a coordination number of six (see Fig. 70*b*); in crystals of ZrO_2 and HfO_2, the coordination numbers of Zr and Hf are seven and eight (Fig. 223*a*).

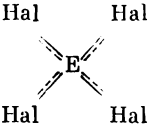
The EO_2 *dioxides* are high-melting, white substances with high enthalpies and Gibbs' energies of formation

	TiO_2	ZrO_2	HfO_2
M. p., °C	1870	2850	2900
$\Delta H^\circ_{f,\,298}$, kJ/mol	—944	—1100	—1118
$\Delta G^\circ_{f,\,298}$, kJ/mol	—889	—1043	—1061

They are quite inert chemically and are insoluble in water, cold dilute acids (except in HF), and alkalis. They react slowly with acids only when heated for a long time, and with alkalis on fusing.

TiO_2 is the most widely used dioxide; because of its chemical inertness, it is employed as a filler for plastics, dyes, and rubbers; ZrO_2 is used in the manufacture of refractory crucibles and as a lining for kilns and furnaces.

The $EHal_4$ *tetrahalides* (except tetrafluoride EF_4) have molecular crystal lattices in the solid state. The stability of their tetrahedral molecules is determined by the π bonds that arise from the free orbitals of the E atoms and unshared electron pairs of the halogen atoms:



This corresponds to the following electron configuration (see Fig. 218):

$$[\sigma]^8\,[\pi]^{10}\,[\pi^{non}]^6$$

The effective charge of the titanium in $TiCl_4$ ($\delta_{Ti} = 0.25$) is therefore lower than that of the carbon atom in CCl_4 ($\delta_C = 0.3$).

The tetrafluorides are polymers. The crystals of TiF_4, for example, are formed by TiF_6 octahedra; the unit cell of ZrF_4 and HfF_4 is an EF_6 octahedron or a square antiprism (Fig. 223*b*).

Almost all the halides (except $TiBr_4$ and EI_4) are colourless. In normal conditions, all the tetrahalides are solids (except liquid $TiCl_4$). The melting point of similar halides rises in the $TiHal_4$ — $ZrHal_4$—$HfHal_4$ series. $TiCl_4$, for example, is a liquid (f.p. —23 °C), while $ZrCl_4$ and $HfCl_4$ melt (under pressure) at roughly 430 °C.

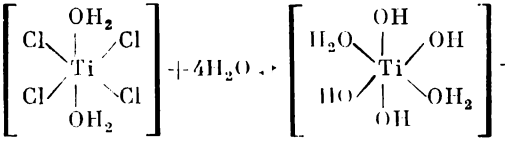
E(IV) halides are usually obtained by heating EO_2 with carbon in an atmosphere of the desired halogen:

$$EO_2 + 2C + 2Cl_2 = ECl_4 + 2CO$$

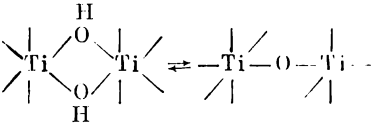
Tetrahalides of molecular structure are volatile and chemically active, tending, for example, to accept donor molecules, and are easily hydrolysed. $TiCl_4$ is the one most commonly used and is employed to obtain metallic titanium. The E(IV) iodides decompose at high temperatures (1000 °C to 1400 °C) into iodine and the metal, a circumstance utilised to obtain especially pure Ti, Zr, and Hf.

The E(IV) *hydroxides* are jelly-like precipitates of variable composition, $EO_2 \cdot nH_2O$. Fresh precipitates (α form) have a relatively large number of OH groups and are therefore more reactive (soluble in acids) than aged ones (β form) in which the -ol groups are replaced by oxol groups. Titanium(IV) hydroxide is soluble in concentrated alkalis; zirconium(IV) and hafnium(IV) hydroxides practically do not react with alkalis.

The hydrated ions Ti^{4+}, Zr^{4+} and Hf^{4+} cannot exist in solution because of their high charges, so that their soluble derivatives are strongly hydrolysed. Hydrolysis proceeds with the formation of various polynuclear complexes. Coordination saturation of $TiCl_4$ to $TiCl_4 \cdot 2H_2O$, with subsequent splitting off of the HCl molecules, can be regarded as the first step in the hydrolysis of $TiCl_4$:



In the next stages polymeric -ol and oxol complexes are formed



The transition from -ol to oxol complexes is easier than the reverse one. The transition from hydroxyaquo complexes to -ol and oxol complexes is promoted by high temperatures, an alkaline medium, and long standing of the solution. Further polymerisation is then also possible, with the result that the polynuclear complexes grow to the size of colloid particles, and free hydroxides ($EO_2 \cdot nH_2O$) can even be isolated.

The molecules of water and OH groups in polynuclear complexes may be replaced by anions present in the solution, which accounts for the complicated composition of the compounds produced in the solution. During the interaction of the oxides or hydroxides with acids, for instance, the corresponding oxy and hydroxy derivatives, for example, of the EOX_2 type (where X = Cl^-, Br^-, I^-, NO_3^-, 1/2 SO_4^{2-}) are produced rather than neutral salts:

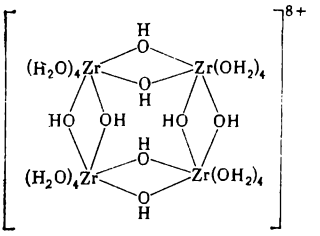
$$Ti(OH)_4 + 2HCl = TiOCl_2 + 3H_2O$$

$$TiO_2 + H_2SO_4 = TiOSO_4 + H_2O$$

Crystal hydrates—$TiOCl_2 \cdot 2H_2O$, $TiOSO_4 \cdot 2H_2O$, $ZrOCl_2 \cdot 8H_2O$, $ZrOSO_4 \cdot 8H_2O$, and $HfOCl_2 \cdot 8H_2O$—are precipitated from acid solutions.

Crystals of $TiOSO_4 \cdot H_2O$ contain endless —Ti—O—Ti—O— chains, which are linked by SO_4^{2-} radicals. The $ZrOCl_2 \cdot 8H_2O$ precipitated from a weak acid

solution contains the tetrameric ion $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$



The zirconium atoms here have a coordination number of eight and are connected through OH bridges; each atom is surrounded by another four water molecules. The oxygen atoms of the water and of the OH groups are located at the apexes of the square antiprism.

Compounds of simple composition are obtained only in nonaqueous solutions. $Ti(SO_4)_2$, for instance, is formed by the interaction of $TiCl_4$ and SO_3 in liquid sulphuryl chloride or by fusing TiO_2 with a disulphate:

$$TiCl_4 + 4SO_3 = Ti(SO_4)_2 + 2SO_2Cl_2$$
$$TiO_2 + 2K_2S_2O_7 = Ti(SO_4)_2 + 2K_2SO_4$$

and $Zr(NO_3)_4$ by the interaction of anhydrous $ZrCl_4$ and N_2O_5.

The halogen derivatives of E(IV) *anion* complexes are relatively simpler in composition and structure (Fig. 224*a*). Fluorocomplexes are the most stable in solution and are easily formed. Thus EO_2 is readily soluble in hydrofluoric acid, and EF_4 is also soluble in solutions of the fluorides of Group I *s* elements:

$$6HF + EO_2 = H_2[EF_6] + 2H_2O$$
$$2KF + EF_4 = K_2[EF_6]$$

The ZrF_6^{2-} ion is a polynuclear complex formed by ZrF_8 octahedral units joined along their edges (see Fig. 223*b*).

Fluorozirconates and fluorohafnates of the $M_3^{+1}[ZrF_7]$ and $M_4^{+1}[ZrF_8]$ type are formed at the same time. The fluorotitanates, fluorozirconates, and fluorohafnates of Group I *s* elements are readily soluble in water.

Derivatives of the other E(IV) anion complexes are usually formed by fusing the appropriate compounds, e.g.

$$2KCl + ECl_4 = K_2ECl_6$$
$$2KOH + EO_2 = K_2EO_3 + H_2O$$
$$CaCO_3 + TiO_2 = CaTiO_3 + CO_2$$

The composition of the oxytitanates(IV), oxyzirconates(IV), and oxyhafnates(IV) formed is quite varied (Fig. 224*b*). The simplest of

them can be described by the formulas $\overset{+2}{M}EO_3$, $\overset{+1}{M}_2EO_3$ and $\overset{+2}{M}_2EO_4$. The structure of oxytitanates often corresponds to the $CaTiO_3$ (perovskite) and $FeTiO_3$ (ilmenite) type (see Fig. 73 and p. 117 respectively). Most oxytitanates, oxyzirconates, and oxyhafnates are mixed oxides insoluble in water; the derivatives of the alkali metals are hydrolysed.

Anion complexes in which the O_2^{2-} peroxide radical acts as a ligand are very characteristic of titanium and its analogues. Peroxyzirco-

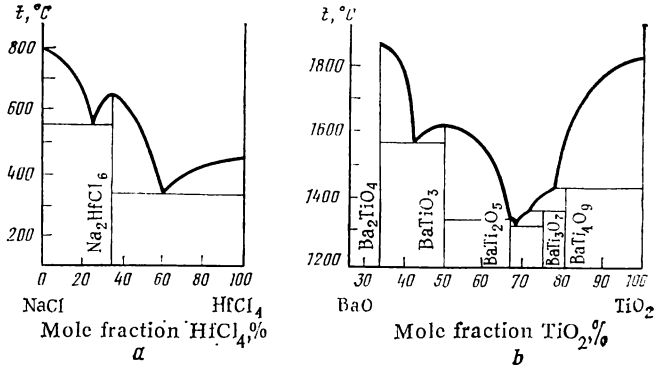


Fig. 224. Phase diagrams of (*a*) $NaCl—HfCl_4$ and (*b*) $BaO—TiO_2$ systems

nates and peroxytitanates are formed by the action of H_2O_2 on the appropriate compounds: e.g.

$$E(SO_4)_2 + H_2O_2 = H_2[E(O_2)(SO_4)_2]$$

The solutions of Ti(IV) compounds then become yellow-orange; this fact is used in analytical chemistry for identifying Ti(IV) compounds and hydrogen peroxide.

Compounds of Ti(III). As already remarked, the +3 oxidation state is clearly expressed only in titanium. Derivatives of Ti(III) are obtained by reducing Ti(IV) compounds: e.g.

$$2TiO_2 + H_2 \xrightarrow{1200\ °C} Ti_2O_3 + H_2O$$

$$2TiCl_4 + H_2 \xrightarrow{650\ °C} 2TiCl_3 + 2HCl$$

During electrochemical or chemical reduction of Ti(IV) compounds in aqueous solution, a violet aquo complex $Ti(OH_2)_6^{3+}$ is formed.

The stable coordination number of Ti(III) is six; its octahedral complexes have the following electron configuration

$$[\sigma]^{12}[\pi_d^{non}]^1$$

The transition of a π_d^{non} electron to the molecular σ_d^* orbital accounts for the colour of the complexes, which is usually violet (at Δ = 2.1-2.5 eV) for Ti(III) compounds (see Fig. 219).

In accordance with the stable coordination number of Ti(III) its violet oxide Ti_2O_3 has a structure of the α-Al_2O_3 type (see Fig. 72), and the violet chloride $TiCl_3$ has a layer structure; in acid solutions there is an aquo complex $[Ti(OH_2)_6]^{3+}$, which is also found in some crystal hydrates and titanium alums $\overset{+1}{M}Ti(SO_4)_2 \cdot 12H_2O$, and accounts for their violet colour.

Ti_2O_3 is practically insoluble in water. The dark violet precipitate of $Ti_2O_3 \cdot nH_2O$, which is obtained by adding an alkali to solutions of Ti(III) salts, is basic and is insoluble in excess alkali.

The derivatives of Ti(III) are reductants. They are easily oxidised, for example, by atmospheric oxygen:

$$4TiCl_3 + O_2 + 2H_2O = 4TiOCl_2 + 4HCl$$

The oxidation of Ti(III) compounds in acid solutions is accompanied with disappearance of their violet colour, because of the formation of Ti(IV) compounds. Compounds of Ti(III) may also undergo disproportionation; thus, when heated to 400 °C, $TiCl_3$ is decomposed as follows:

$$2\overset{+3}{Ti}Cl_3\,(c) = \overset{+2}{Ti}Cl_2\,(c) + \overset{+4}{Ti}Cl_4\,(g)$$

It is easy to demonstrate that this reaction is endothermic (ΔH°_{298} = = 142 kJ), but is accompanied with a marked increase in the entropy (ΔS°_{298} = 171 J/K) since one of the reaction products is a gas. When heated further, $TiCl_2$ also undergoes disproportionation:

$$2\overset{+2}{Ti}Cl_2\,(c) = \overset{0}{Ti}\,(c) + \overset{+4}{Ti}Cl_4\,(g)$$

Although this reaction is even more endothermic (ΔH°_{298} = = 274 kJ), the increase in entropy of 155 J/K makes the process realizable but only at higher temperatures.

Compounds of Zr(III) and Hf(III) have not been studied in detail.

CHAPTER 4

Group V *d* Elements

The *d* elements of Group V—vanadium V, niobium Nb, tantalum Ta, and nielsbohrium Ns*—form the vanadium subgroup. Their

* Nielsbohrium has been synthesised artificially (see p. 660). The name is disputed. Another name for this element is hahnium Ha.

main characteristics are as follows:

	$_{23}V$	$_{41}Nb$	$_{73}Ta$
Atomic mass	50.942	92.906	180.948
Valence electrons	$3d^34s^2$	$4d^45s^1$	$5d^36s^2$
Metal atom radius, nm	0.134	0.145	0.146
Conventional ion E^{5+} radius, nm	0.040	0.066	0.066
Ionisation energy $E^0 \rightarrow E^+$, eV	6.74	6.88	7.89
Abundance, mole per cent	6×10^{-3}	2×10^{-4}	1.8×10^{-5}
Natural isotopes	^{51}V (99.75%) ^{52}V (0.25%)	^{93}Nb (100%)	^{181}Ta (99.99%) ^{180}Ta (0.01%)

In contrast to the arsenic subgroup, the electron shells of atoms in the vanadium subgroup become denser with increasing atomic number of the elements as is shown by the increasing first ionisation energies and the character of the changes in atomic and ionic radii in the V—Nb—Ta series. Because of lanthanide contraction, the atomic and ionic radii of Nb and Ta are practically the same, so that they are closer to each other in properties than to vanadium.

The oxidation states of vanadium in its compounds are +2, +3, +4, and +5. The most stable oxidation state of niobium and tantalum, like of the other 4*d* and 5*d* elements, is their highest oxidation

Table 47. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of Elements of the Vanadium Subgroup**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical examples
+2	d^3	6	Octahedron	$[V(OH_2)_6]^{2+}$, VO, VF_2
+3	d^2	4	Tetrahedron	$[VCl_4]^-$
		6	Octahedron	$[V(OH_2)_6]^{3+}$, $[VF_6]^{3-}$, V_2O_3, VF_3
+4	d^1	4	Tetrahedron	VCl_4
		6	Octahedron	EO_2, $[VO(OH_2)_5]^{2+}$
+5	d^0	4	Tetrahedron	$VOCl_3$
		5	Trigonal bipyramid	VF_5
		6	Octahedron	NbF_5, TaF_5, ECl_5, $NbOCl_3$, $[VF_6]^-$, $NaNbO_3$, $NaTaO_3$
		7	See Fig. 226	$[NbF_7]^{2-}$, $[TaF_7]^{2-}$, $[NbOF_6]^{3-}$
		8	Square antiprism	$[TaF_8]^{3-}$

state, +5. The highest oxidation state of vanadium is stabilised in its fluorine and oxy derivatives.

Stable coordination numbers of vanadium and its analogues corresponding to their respective oxidation states are given in Table 47.

4.1. Vanadium Subgroup

Vanadium is more abundant than copper, zinc, or lead, but its compounds do not form large deposits. It is dispersed in various silicate and sulphide ores. Its most important minerals are *patronite* $VS_{2-2.5}$, *sulvanite* Cu_3VS_4, *alaite* $V_2O_3 \cdot H_2O$, and *vanadinite* $Pb_5(VO_4)_3Cl$. Niobium and tantalum almost always occur together, as a rule in niobate-tantalate minerals of a $\overset{+2}{M}E_2O_6$ composition (M = = Fe, Mn). When tantalum predominates in the mineral it is called *tantalite*, $\overset{+2}{M}(TaO_3)_2$, and when niobium predominates *columbite* $M(NbO_3)_2$.

The simple substances. As simple substances, V, Ta, and Nb are grey, high-melting metals with a body-centred cubic lattice. Some of their constants are as follows:

	V	Nb	Ta
Density, g/cm³	5.96	8.57	16.6
M. p., °C	1920	~ 2470	~ 3000
B. p., °C	~ 3400	~ 4900	~ 5400
S°_{298}, J/K·mol	28.9	36.6	41.5
$\Delta H^\circ_{\text{subl., 298}}$, kJ/mol	515	742	775
Electrical conductivity	4	5	6

The physicochemical properties of vanadium, niobium, and tantalum depend essentially on their purity. The pure metals, for example, are ductile, but admixtures (especially O, H, N, and C) greatly reduce their plasticity and increase their hardness.

In normal conditions V, and especially Nb and Ta, are very stable chemically. Only aqua regia and concentrated HF can dissolve vanadium in the cold, and HNO_3 and concentrated H_2SO_4 with heating. Niobium and tantalum are soluble in a mixture of HF and HNO_3 with the formation of anion fluorine complexes corresponding to the highest oxidation states of the elements

$$\overset{0}{3Ta} + 5HNO_3 + 21HF = 3H_2[\overset{+5}{TaF_7}] + 5NO + 10H_2O$$

Vanadium, niobium, and tantalum also react with fused alkalis in the presence of oxidants, i.e. in conditions promoting the formation of oxyanion complexes corresponding to their highest oxidation states

$$\overset{0}{4E} + 5O_2 + 12KOH \xrightarrow{\text{fusion}} 4K_3[\overset{+5}{EO_4}] + 6H_2O$$

When heated, the metals are oxidised by oxygen to E_2O_5, and by fluorine to EF_5. At high temperatures they also react with chlorine, nitrogen, carbon, etc.

Vanadium, niobium, and tantalum are obtained from their natural compounds by converting them first into their oxides, or into simple or complex halides, with subsequent reduction by a metallothermic method:

$$E_2O_5 + 5Ca = 5CaO + 2E$$
$$K_2[EF_7] + 5Na = 2KF + 5NaF + E$$

Tantalum is also obtained by electrolysis of Ta_2O_5 in molten complex fluorides $K_2[TaF_7]$.

Niobium is difficult to separate from tantalum because of the similarity of their properties. Metals of special purity are obtained by thermal decomposition of their iodides. Industrial metals are usually obtained in the form of *ferrovanadium*, *ferroniobium*, and *ferrotantalum*.

The steel industry is the main consumer of vanadium. The valuable physicochemical properties of V, Nb, and Ta make them useful in building nuclear reactors. Niobium, and even more so tantalum, present great interest as engineering materials for highly agressive media in the chemical industry.

4.2. Compounds of the Vanadium Subgroup Elements

Metallic and metal-like compounds. Powdered vanadium, niobium, and tantalum can absorb considerable amounts of hydrogen, oxygen, and nitrogen to form interstitial solid solutions in which the nonmetals are converted to the atomic state, and their electrons are involved in building the *d* zone of the metal crystal. The solubility of the nonmetals increases with heating and the character of the bond and properties of the resulting compounds alter accordingly. Thus the oxidation of Nb (and of V and Ta) by oxygen proceeds in the following steps

$$Nb + O_2 \rightarrow Nb \underset{\text{solution}}{\underset{|}{-}} O \rightarrow Nb_6O \rightarrow Nb_2O \rightarrow NbO \rightarrow NbO_2 \rightarrow Nb_2O_5$$

Nb_6O and Nb_2O are typical metallic compounds in their properties. NbO (grey) has a varying composition ($NbO_{0.94-1.04}$), a metallic lustre, and metallic conductivity. The dioxide NbO_2 (black) also has a variable composition ($NbO_{1.9-2.09}$) but is a semiconductor. Nb_2O_5, finally, has a more or less stable composition and does not possess electron conductivity. Thus, as the oxygen content rises, the proportion of metallic linkages falls and of covalent bonds increases, which accounts for the changes in the oxides' properties.

The *hydrides* of vanadium and its analogues EH are brittle, grey or black metal-like powders with a varying composition, chemically stable, not reacting with either water or dilute acids.

The *nitrides* (EN, Nb_2N, Ta_2N), *carbides* (EC, E_2C), *borides* (EB, EB_2, E_3B_4), and certain other compounds with inactive nonmetals also have high corrosion resistance.

Vanadium, niobium, and tantalum react with each other and with metals close to them in the periodic system (of the iron, titanium, and chromium subgroups) to form metallic solid solutions. As the difference in electron structure of the reacting metals becomes greater, the possibility of getting solid solutions diminishes, while the conditions for the forming of intermetallic compounds like Co_3V, Fe_3V, Ni_3V, Al_3V, etc., improve.

Then intermetallic compounds impart valuable physicochemical properties to metal alloys. Vanadium, for example, greatly increases the strength, toughness, and wear resistance of steels. Niobium gives steels increased resistance to corrosion and high temperatures. For these reasons most of the vanadium and niobium produced is used in the steel industry for making tool and engineering steels.

Alloys based on carbides, nitrides, borides, and silicides of niobium and tantalum present great interest since they possess extraordinary hardness, chemical inertness, and heat resistance.

Compounds of vanadium (II), niobium (II) and tantalum(II). Vanadium compounds are the stablest derivatives in which the elements of this subgroup have an oxidation state of +2. The coordination number of vanadium(II) is six, which corresponds to an octahedral structure of its complexes (unit cells) in compounds.

Vanadium(II) oxide VO ($VO_{0.9}$—$VO_{1.3}$) has a crystal lattice of NaCl type. It is black, with a metallic lustre, and relatively high electrical conductivity. VO is prepared by reducing V_2O_5 in a stream of hydrogen. It does not react with water but, being a basic compound, reacts readily with dilute acids:

$$VO + 2OH_3^+ + 3H_2O = [V(OH_2)_6]^{2+}$$

The $[V(OH_2)_6]^{2+}$ ion is violet and so are the crystal hydrates, for example, $M^{+1}_2SO_4 \cdot VSO_4 \cdot 6H_2O$, $VSO_4 \cdot 7H_2O$, and $VCl_2 \cdot 6H_2O$.

The compounds of V(II) are strong reductants. The violet solutions of $[V(OH_2)_6]^{2+}$ derivatives are readily oxidised to $[V(OH_2)_6]^{3+}$, and become green. In the absence of oxidants (for example, atmospheric oxygen) solutions of V(II) compounds gradually decompose water with liberation of hydrogen.

Derivatives of Nb(II) and Ta(II) are cluster type compounds (see below, p. 556).

Compounds of vanadium(III), niobium(III) and tantalum(III). The coordination number of vanadium(III) is six. Its compounds are similar in properties to the corresponding aluminium(III) compounds. Black vanadium(III) oxide V_2O_3 has a crystal lattice of the corundum α-Al_2O_3 type (see Fig. 72). It has a variable $VO_{1.60-1.80}$ composition. Alkaline solutions of V(III) compounds liberate a green hydroxide $V(OH)_3$ of variable composition $V_2O_3 \cdot nH_2O$. These compounds are amphoteric but with predominantly basic properties; V_2O_3 and $V_2O_3 \cdot nH_2O$, for instance, are soluble in acids:

$$V_2O_3 + 6OH_3^+ + 3H_2O = 2[V(OH_2)_6]^{3+}$$

The aquo complexes of $[V(OH_2)_6]^{3+}$ and their derivatives (crystal hydrates $VCl_3 \cdot 6H_2O$, $VI_3 \cdot 6H_2O$) are green. The vanadium alums $M^{+1}[V(SO_4)_2] \cdot 12H_2O$ are violet in the solid state but yield green solutions.

Vanadium trihalides $VHal_3$ are crystalline solids; the trichloride VCl_3 has a layer structure (see Fig. 232*a*). Vanadium trihalides react with the corresponding basic halides to form halogen vanadates, derivatives of the $[VHal_6]^{3-}$ and $[V_2Cl_9]^{3-}$ ions (see Fig. 61*c*):

$$3KF + VF_3 = K_3[VF_6], \quad 3KCl + 2VCl_3 = K_3[V_2Cl_9]$$

Derivatives of vanadium(III) are strong reductants and are easily oxidised in solution by atmospheric oxygen to derivatives of V(IV). When heated, the trihalides undergo disproportionation:

$$2VCl_3\,(s) = VCl_2\,(s) + VCl_4\,(g)$$

The reaction is endothermic and proceeds because of the entropy factor (owing to the formation of volatile VCl_4).

Derivatives of Nb(III) and Ta(III) are mainly cluster compounds (see below, p. 556).

Compounds of vanadium(IV), niobium(IV) and tantalum(IV). In normal conditions, an oxidation state of +4 is more typical of vanadium. Compounds of vanadium(III) are easily oxidised by molecular oxygen to V(IV) derivatives, while compounds of V(V) are reduced to V(IV) derivatives. The stablest coordination number of vanadium(IV) is six; the coordination numbers four and five are also stable.

Blue VO_2 ($VO_{1.8-2.17}$), brown VF_4, red-brown liquid VCl_4, and also $VOHal_2$ oxyhalides are known for vanadium(IV). The dioxide VO_2 is formed by carefully reducing V_2O_5 by hydrogen; VCl_4 is obtained by the interaction of hot V_2O_5 and CCl_4 or by oxidising vanadium (or ferrovanadium) by chlorine.

The crystal lattice of the dioxide VO_2 is of the rutile TiO_2 type (see Fig. 70*b*). The molecule of VCl_4, like that of $TiCl_4$, has a tetrahedral structure.

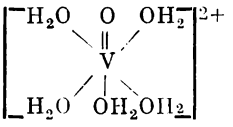
Compared with similar compounds of V(II) and V(III), the binary compounds of V(IV) have more pronounced acidic properties. Thus, water-insoluble VO_2 reacts relatively readily with alkalis on heating to form brown oxyvanadates(IV), usually with a $M_2[V_4O_9]$ composition:

$$4VO_2 + 2KOH = K_2[V_4O_9] + H_2O$$

It is dissolved even more easily in acids to form light blue aquo derivatives of *oxyvanadyl* VO^{2+} (rather than aquo complexes of V^{4+}):

$$VO_2 + 2H^+ + 4H_2O = [VO(OH_2)_5]^{2+}$$

The VO^{2+} oxyvanadyl grouping is very stable since the VO bond is close to double:



The interatomic distance d_{VO} in the vanadyl grouping is 0.167 nm, while the distance d_{V-OH_2} is 0.23 nm.

The VO^{2+} grouping remains unaltered in various reactions and, depending on the nature of the ligands, can be constituent of either cation or anion complexes, and also of neutral molecules.

An interaction of $VHal_4$ and basic halides is not characteristic, but derivatives of oxyvanadyl anion complexes, of the $K_2[VOF_4]$ and $(NH_4)_3[VOF_5]$ type, are very typical of vanadium(IV).

Vanadium tetrahalides are easily hydrolysed; VCl_4, for instance, is instantaneously converted into $VOCl_2$ (vanadyl dichloride) in water:

$$VCl_4 + H_2O = VOCl_2 + 2HCl$$

Dioxides EO_2, tetrahalides $EHal_4$, and oxydihalides $EOHal_2$ are known for niobium and tantalum. It is supposed that these compounds have metal-metal bonds, i.e. are cluster compounds (see below, p 556).

The tendency to use all their valence electrons characteristic of niobium and tantalum is usually realised through their transition to their highest, +5 oxidation state. At lower oxidation states this tendency is realised through the formation of M—M bonds (see p. 557).

Compounds of vanadium(V), niobium(V) and tantalum(V). The stability of compounds increases in the V(V)—Nb(V)—Ta(V) series as is shown, for example, by the Gibbs' energies of formation of similar compounds: e.g.

	V_2O_5 (c)	Nb_2O_5 (c)	Ta_2O_5 (c)
$\Delta G^\circ_{f,\,298}$, kJ/mol	−1427	−1776	−1908

Only the oxide V_2O_5 and fluoride VF_5 are known for vanadium(V) while all other ($EHal_5$) halides are known for niobium(V) and tantalum(V). Oxyhalides $EOHal_3$ are also known for E(V). All these compounds are typically acidic. Certain of their anion complexes are the following:

EF_5	EOF_3	E_2O_5
$[EF_6]^-$	$[EOF_5]^{2-}$	$[EO_4]^{3-}$, $[EO_3]^-$
$[NbF_7]^{2-}$, $[TaF_7]^{2-}$	$[NbOF_6]^{3-}$, $[TaOF_6]^{3-}$	
$[NbF_8]^{3-}$, $[TaF_8]^{3-}$		

Coordination numbers of four and six are most typical of vanadium(V), and six and seven of Nb(V) and Ta(V), but there are com-

pounds in which the coordination numbers of the last two are as high as eight.

The *oxides*, red V_2O_5 (m.p. 670 °C), white Nb_2O_5 (m.p. 1490 °C) and Ta_2O_5 (m.p. 1870 °C) are high-melting crystalline solids. The unit cell of E_2O_5 is an EO_6 octahedron. (In V_2O_5 the VO_6 octahedron is strongly distorted, almost to a trigonal bipyramid by an additional oxygen atom.) The oxides have high heats and Gibbs' energies of formation. Because of lanthanide contraction, the values of ΔH_f° and ΔG_f° for Nb_2O_5 and Ta_2O_5 are close, and differ markedly from those for V_2O_5.

Vanadium(V) oxide is obtained by thermal decomposition of NH_4VO_3:

$$2NH_4VO_3 = V_2O_5 + 2H_3N + H_2O$$

It is very weakly soluble in water (about 0.007 g/litre at 25 °C) to form a pale yellow acidic solution; V_2O_5 is readily soluble in alkalis, and is soluble in acids only after prolonged heating. The oxides of Nb(V) and Ta(V) are chemically inert, practically insoluble in water and acids, and react with alkalis only in the molten state:

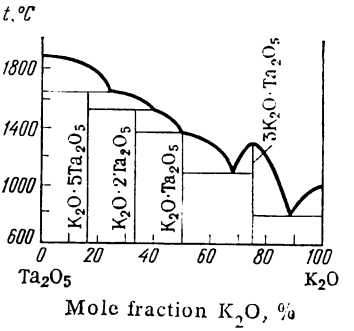


Fig. 225. Phase diagram of the Ta_2O_5—K_2O system

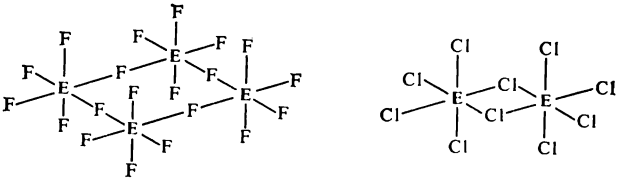
$$E_2O_5 + 2KOH = 2KEO_3 + H_2O$$

Oxyvanadates(V), oxyniobates(V), and oxytantalates(V) are crystalline substances with a complex composition and structure, as will be seen from Fig. 225. Compounds of the $\overset{+1}{M}EO_3$ and $\overset{+1}{M}_3EO_4$ type are the simplest. Most oxyvanadates(V), and especially oxyniobates(V) and oxytantalates(V), are polymers; $NaNbO_3$, for instance, crystallises into a perovskite type structure (see Fig. 73), while $Fe(NbO_3)_2$ and $Mn(TaO_3)_2$ are mixed oxides with a rutile type structure (see Fig. 70*b*). Only the derivatives of Group I *s* elements and NH_4^+ are soluble in water. The most important vanadate is NH_4VO_3, which is used for obtaining other vanadium compounds.

Acids in acting on solutions of oxyvanadates, cause polymerization of the vanadate ions up to the formation of hydrated oxides $V_2O_5 \cdot nH_2O$. The change in the composition of vanadate ions involves a change in their colour (from almost colourless VO_4^{3-} to orange $V_2O_5 \cdot nH_2O$).

$EHal_5$ pentahalides have an insular structure and are therefore low-melting and volatile. They are soluble in organic solvents and are chemically active. The fluorides are colourless, while the other halides are coloured.

Crystalline NbF_5 (m.p. 80 °C, b.p. 235 °C) and TaF_5 (m.p. 95 °C, b.p. 229 °C) consist of tetrameric molecules $(EF_5)_4$, while ECl_5 and EBr_5 (m.p. and b.p. of the order of 200 °C to 300 °C) consist of dimeric $(EHal_5)_2$ molecules:



VF_5 is a viscous liquid (m.p. 19.5 °C) with a structure like that of SbF_5.

Being acidic compounds, the pentahalides are easily hydrolysed to form amorphous precipitates of hydrated oxides:

$$2EHal_5 + 5H_2O = E_2O_5 + 10HHal$$

The pentafluorides and pentachlorides of Nb and Ta, in addition, react with the corresponding basic halides to form $[EF_6]^-$ anion

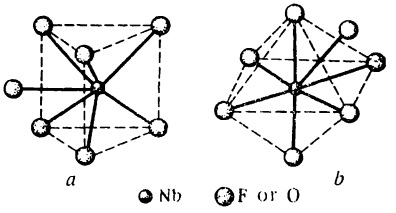


Fig. 226. Structure of (*a*) NbF_7^{2-} and (*b*) $NbOF_6^{3-}$ ions

complexes, and in the case of Nb(V) and Ta(V) $[EF_7]^{2-}$, $[EF_8]^{3-}$ and $[ECl_6]^-$ complex ions as well, for example,

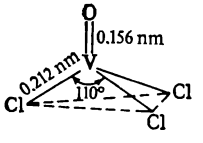
$$KF + VF_5 = K[VF_6]$$

$$2KF + TaF_5 = K_2[TaF_7]$$

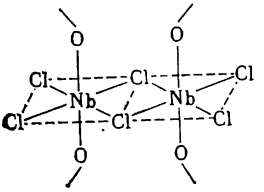
The structure of the $[EF_7]^{2-}$ and $[EF_8]^{3-}$ ions is shown in Fig. 226.

The *oxyhalides* $EOHal_3$ are mostly volatile solids, but $VOCl_3$ is a liquid (f.p. −77 °C, b.p. 127 °C).

The structure of $VOCl_3$ is a distorted tetrahedron with the vanadium atom at the centre



The dimeric groups Nb_2Cl_6 are linked by Nb—O—Nb bridges into endless chains of NbO_2Cl_4 octahedra to form the lattice of $NbOCl_3$



The oxyhalides are easily hydrolysed to form hydrated oxides $E_2O_5 \cdot nH_2O$ and HHal

$$2EOHal_3 + 3H_2O = E_2O_5 + 6HHal$$

and interact with basic halides (Fig. 227) to form anion complexes with a $[VOF_5]^{2-}$ composition; Nb(V) and Ta(V) also form $[EOCl_4]^-$, $[EOHal_5]^{2-}$, and $[EOF_6]^{3-}$ anion complexes (when Hal = F and Cl):

$$2KF + VOF_3 = K_2[VOF_5]$$
$$3KF + NbOF_3 = K_3[NbOF_6]$$

Nb_2O_5 reacts with aqueous solutions containing KF and HF to yield $K_2[NbOF_5]$, while Ta_2O_5 forms $K_2[TaF_7]$:

$$Nb_2O_5 + 4KF + 6HF = 2K_2[NbOF_5] + 3H_2O$$
$$Ta_2O_5 + 4KF + 10HF = 2K_2[TaF_7] + 5H_2O$$

The difference in solubility of $K_2[TaF_7]$ and $K_2[NbOF_5]$ is the basis in a method of separation of niobium and tantalum.

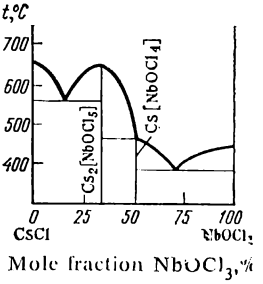


Fig. 227. Phase diagram of the CsCl—$NbOCl_3$ system

Peroxy complexes, like yellow $[VO_2(O_2)_2]^{3-}$, blue-violet $[V(O_2)_4]^{3-}$, and colourless $[Nb(O_2)_4]^{3-}$ and $[Ta(O_2)_4]^{3-}$ are quite typical of vanadium(V) and its analogues. $[E(O_2)_4]^{3-}$ complexes have a dodecahedral structure (Fig. 223).

The peroxyvanadates, peroxyniobates and peroxytantalates are formed by the action of hydrogen peroxide on the corresponding compounds of E(V) in an alkaline medium: e.g.

$$VO_4^{3-} + 2H_2O_2 = [VO_2(O_2)_2]^{3-} + 2H_2O$$
$$E_2O_5 + 8H_2O_2 + 6KOH = 2K_3[E(O_2)_4] + 11H_2O$$

These compounds are stable in the solid state. Peroxyvanadates are decomposed by the action of acids, while peroxyniobates and peroxytantalates are converted into corresponding peracids of an HEO_4 composition.

Derivatives of vanadium(V) have oxidising properties in an acid medium, oxidising concentrated hydrochloric acid, for example:

$$V_2O_5 + 6HCl \rightleftharpoons 2VOCl_2 + Cl_2 + 3H_2O$$

Powerful reducing agents and heating are required to transfer Nb(V) and especially Ta(V) to lower oxidation states.

Vanadium compounds are employed in the chemical industry as catalysts (in the production of sulphuric acid), and also in the glass and other industries.

CHAPTER 5

Group VI *d* Elements

Chromium Cr, molybdenum Mo, and tungsten W are *d* elements of Group VI forming the chromium subgroup

	$_{24}$Cr	$_{42}$Mo	$_{74}$W
Atomic mass	52.01	95.95	183.92
Valence electrons	$3d^54s^1$	$4d^55s^1$	$5d^46s^2$
Metallic atom radius, nm	0.127	0.139	0.140
Conventional ion E^{6+} radius, nm	0.035	0.065	0.065
Ionisation energy, $E^0 \rightarrow E^+$, eV	6.77	7.10	7.98
Abundance, mole per cent	8×10^{-3}	6×10^{-5}	1×10^{-5}

As will be seen from this table, the ionisation energy increases in the Cr—Mo—W series, i.e. the electron shells of the atoms are compacted, which is particularly pronounced in the transition from Mo to W. Because of lanthanide contraction, the latter has atomic and ionic radii similar to those of Mo; tungsten and molybdenum are therefore closer to each other in properties than to chromium.

The characteristic oxidation states of chromium are +3 (corresponding to the stable nonbonding d^3 electron configuration) and, to a lesser extent, +6. The highest oxidation state +6 is most typical of molybdenum and tungsten (as of other 4*d* and 5*d* elements). Compounds in which chromium and its analogues have oxidation states of 0, +1, +2, +4, and +5 are also possible.

Coordination numbers of six and four are most typical of chromium, molybdenum, and tungsten, but derivatives are also known in which the coordination number of Mo and W is as high as eight. The oxidation states of the elements and corresponding coordination numbers are given in Table 48.

Like other *d* elements, Cr, Mo and W predominantly form cation complexes in their lower oxidation states, and anion complexes in

Table 48. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of Chromium Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration of complex	Typical compounds
0	d^6	6	Octahedron	$E(CO)_6$
+2	d^4	6	Distorted octahedron	$[Cr(OH_2)_6]^{2+}$, CrF_2, $CrCl_2$, $MoCl_2$, WCl_2
		9		
+3	d^3	6	Octahedron	$[Cr(OH_2)_6]^{3+}$, $[CrCl_6]^{3-}$, Cr_2O_3, $CrCl_3$
+6	d^0	4	Tetrahedron	$[EO_4]^{2-}$, EO_2Cl_2, CrO_3
		6	Octahedron	$EHal_6$, MoO_3, WO_3, $[MoO_2F_4]^{2-}$, $[WO_3F_3]^{3-}$
		8	?	$[MoF_8]^{2-}$, $[WF_8]^{2-}$

higher oxidation states.* Thus, both cation and anion complexes are possible with Cr(III), while anion complexes are typical of Cr(VI), Mo(VI), and W(VI); CrO, for example, is a basic oxide, Cr_2O_3 is amphoteric, while CrO_3 is an acidic oxide.

5.1. Chromium Subgroup

Natural chromium consists of four stable isotopes, molybdenum of seven, and tungsten of five. Many radioactive isotopes have been obtained artificially.

The most important minerals of these elements are *chromite* $Fe(CrO_2)_2$, *molybdenite* MoS_2, *scheelite* $CaWO_4$, and *wolframite* $(Fe, Mn)WO_4$.

The presence of traces of molybdenum in soil is vital for the normal growth of plant organisms, especially for leguminous plants. Molybdenum compounds probably act as a catalyst in the fixation of atmospheric nitrogen.

The simple substances. Chromium, molybdenum, and tungsten are greyish-white, shiny metals. The allotropes of Cr, Mo, and W are stable in normal conditions and have a body-centred cubic structure. Their principal constants are as follows:

	Cr	Mo	W
Density, g/cm³	7.2	10.2	19.3
M.p., °C	1890	2620	3380
B.p., °C	3390	4800	5900
Electrical conductivity	7.1	20.2	19.3
$\Delta H^\circ_{subl.,\,298}$, kJ/mol	368	669	878

* Complexes with ligands of CO or CN^- type, which stabilise lower oxidation states, are not meant here (see p. 551).

Tungsten is the most refractory of all metals. Melting points and heats of atomisation (sublimation) rise in the Cr—Mo—W series, owing to strengthening of the covalent bond (formed by *d* electrons) in the metal crystal. Admixtures greatly affect the properties of the metals. Commercial chromium, for example, is one of the hardest metals, while pure chromium is plastic.

As with the other subgroups of *d* elements, chemical activity decreases significantly in the Cr—Mo—W series with increasing atomic numbers; chromium, for instance, displaces hydrogen from dilute HCl and H_2SO_4, while tungsten is soluble only in a hot mixture of HF and HNO_3:

$$\overset{0}{E} + 21HNO_3 + 8HF = H_2\overset{+6}{[EF_8]} + 2NO + 4H_2O$$

Because of the formation of EO_4^{2-} anion complexes, molybdenum and tungsten interact with fused alkalis in the presence of an oxidant:

$$\overset{0}{E} + 3\overset{+5}{NaNO_3} + 2NaOH = \overset{+6}{Na_2EO_4} + 3\overset{+3}{NaNO_2} + H_2O$$

Chromium is passivated in concentrated HNO_3 and H_2SO_4. When heated (particularly in the powdered state), Cr, Mo, and W are quite readily oxidised by many nonmetals, burning, for example, in oxygen

$$2Cr\ (c) + 3/2O_2\ (g) = Cr_2O_3\ (c), \qquad \Delta G^\circ_{298} = -1059\ kJ$$

$$Mo\ (c)\ (W) + 3/2O_2\ (g) = MoO_3\ (c)\ (WO_3), \qquad \Delta G^\circ_{298} = -668\ (-767)\ kJ$$

to form oxides of chromium(III), molybdenum(VI), and tungsten(VI), which corresponds to their stable oxidation states. The formation of CrO_3 is less advantageous thermodynamically than Cr_2O_3 ($\Delta G^\circ_{f,298} = -506$ kJ/mol).

Chromium is easily passivated and is therefore used for electroplating and in making corrosion-resistant steels. Molybdenum is used in the manufacture of chemical apparatus, and tungsten in electrical engineering (in particular, in the manufacture of incandescent lamps). Molybdenum and tungsten are also used as catalysts.

Relatively pure chromium is obtained by aluminothermy

$$Cr_2O_3\ (c) + 2Al\ (c) = 2Cr\ (c) + Al_2O_3\ (c), \qquad \Delta G^\circ_{298} = -523\ kJ$$

while molybdenum and tungsten are obtained by reducing their oxides by hydrogen. Tungsten is now mostly obtained by the reaction of its halides with hydrogen in the gaseous phase at 1200 °C.

For the steel industry chromium is obtained as its alloy with iron (*ferrochrome*, containing up to 60 per cent Cr) by reducing chromite by carbon in an electric furnace:

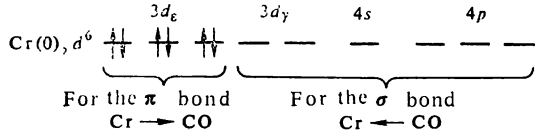
$$\overset{+2}{Fe}\,(\overset{+3}{Cr}O_2)_2 + 4\overset{0}{C} = \overset{0}{Fe} + 2\overset{0}{Cr} + 4\overset{+2}{CO}$$

Ferromolybdenum and *ferrotungsten* are used for making high-grade steels.

5.2. Compounds of the Chromium Subgroup Elements

Compounds of chromium(0), molybdenum(0), and tungsten(0). A zero oxidation state of *d* elements is exhibited in compounds with σ donor and π acceptor ligands, e.g. with CO molecules. Hexacarbonyls $E(CO)_6$ are known for chromium and its analogues. These are colourless easily sublimated solids (m.p. 150 °C to 170 °C), with diamagnetic molecules and an octahedral configuration with the *d* element atom at the centre.

The atoms of chromium and its analogues in the zero oxidation state can be described by a d^6 electron configuration:



The CO molecule has the following electron configuration (see Table 40):

$$[\sigma_s]^2\,[\sigma_s^*]^2\,[\pi_{x,\,y}]^4\,[\sigma_z]^2\,[\pi_{x,\,y}^*]^0\,[\sigma_z^*]^0$$

Two occupied σ_s orbitals correspond to two nonbonding electron pairs, one of which belongs to the carbon and the other to the oxygen atom.

Six free $3d^2_\gamma 4s4p^3$ orbitals of Cr(0) and electron pairs of the carbon atom of six CO molecules form six σ bonds Cr—CO (Fig. 228). The

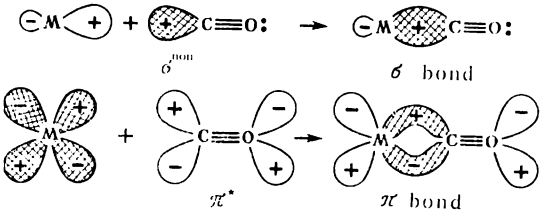


Fig. 228. Scheme of the formation of M—CO σ and π bonds in the carbonyls of *d* elements. Shaded orbitals contain electrons; unshaded ones are vacant

$Cr(CO)_6$ molecule is stabilised by a π dative Cr → CO interaction in which $3d_\varepsilon$ electron pairs of the chromium atom and unoccupied π^* orbitals of the CO molecules are involved (Fig. 228). Because of the transfer of charge from CO to the chromium atom (with the σ donor-acceptor interaction) and from the Cr atom to the CO molecule (with the π dative interaction) the resulting charge on the chromium atom becomes positive $\delta_{Cr} = 0.4+$.

The transfer of the charge during the formation of the M ← CO σ bond and M → CO π bond reduces bond order in the CO molecule. According to the infrared spectrum, the frequency of valence oscillations for a free CO molecule is $\tilde{\nu}_{CO} = 2155\ cm^{-1}$, while it is about 2000 cm^{-1} for the coordinated CO groups.

The carbonyls of *d* elements (see Table 49) are liquids or crystalline solids, readily soluble in organic solvents. Like CO, they are *extremely toxic.* Very pure metals are refined by the thermal decomposition of carbonyls. Carbonyls are also used in chemical synthesis. Those of metals are synthesised by various techniques. Nickel, iron, and cobalt react directly with carbon(II) oxide to yield the appropriate carbonyls, while carbonyls of other metals are usually obtained by reduction of the corresponding salts or metal complexes in the presence of CO.

Table 49. **Selected Binary Carbonyls of *d* Elements of Groups VI, VII, and VIII**

VI	VII	VIII		
d^6	d^7	d^8	d^9	d^{10}
$Cr(CO)_6$, colourless, sublimes	$Mn_2(CO)_{10}$, yellow, m.p. 155°C, sublimes	$Fe(CO)_5$, yellow, f.p. —20°C, b.p. 103°C	$Co_2(CO)_8$, orange-red, m.p. 51°C	$Ni(CO)_4$, colourless, f.p. —19°C, b.p. 43°C
$Mo(CO)_6$, colourless, sublimes	$Tc_2(CO)_{10}$, colourless, m.p. 160°C	$Ru(CO)_5$, colourless, f.p. —22°C	$Rh_2(CO)_8$, orange, m.p. 76°C	—
$W(CO)_6$, colourless, sublimes	$Re_2(CO)_{10}$, colourless, m.p. 177°C, sublimes	$Os(CO)_5$, colourless, f.p. —15°C	$Ir_2(CO)_8$, green-yellow, sublimes	—

Mononuclear, dinuclear, and polynuclear carbonyls are known. The mononuclear ones are formed by *d* elements with an even number of valence electrons; *d* elements with an odd number of valence electrons form dinuclear carbonyls of the cluster type with an M—M bond. Other carbonyls of the cluster type are less known, e.g. $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$, $Rh_6(CO)_{16}$.

As already indicated, the N_2 molecule has much in common with the CO molecule as regards its properties. The nitrogen molecule, for example, is capable of a σ donor and π acceptor dative interaction and can act as a ligand in complex compounds. Compounds, *nitrogenyls*, in which nitrogen molecules act as ligands, are of great practical and theoretical interest, e.g. $[Ru(NH_3)_5(N_2)]Cl_2$. $[(NH_3)_5RuN_2Ru(NH_3)_5]Cl_4$.

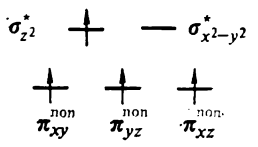
The formation of complexes with N_2 ligands is very important in the fixation of atmospheric nitrogen by microorganisms, and in the catalytic synthesis of ammonia. In natural conditions (i.e. at normal temperatures and pressure) the biochemical fixation of atmospheric nitrogen probably involves the formation of complexes with iron and molybdenum.

Compounds of chromium(II), molybdenum(II), and tungsten (II). A coordination number of six is typical of chromium in the +2 oxidation state. This corresponds, as a rule, to the formation of

high-spin complexes (and unit cells) with an electron configuration of

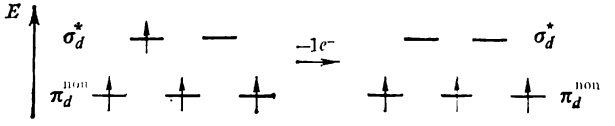
$$[\sigma]^{12}\,[\pi_d^{non}]^3\,[\sigma_d^*]^1$$

Since only one of the two orbitals at the σ_d^* level is occupied



the high-spin octahedral complexes are distorted geometrically: two ligands being at greater distances than the other four. In a crystal of $CrCl_2$, for example, four chlorine atoms are 0.239 nm away from the chromium(II) atom, while the other two are 0.290 nm away.

When an electron is removed from the antibonding orbital, a specially stable configuration $(\sigma)^{12}\,(\pi_d^{non})^3$ arises:



Compounds of chromium(II) are therefore strong reductants.

Only a few binary compounds, e.g. the dihalides $CrHal_2$, are known for chromium(II). It is very difficult to obtain chromium(II) oxide CrO (black) and its very existence is doubted.

The binary compounds of chromium(II), and also $Cr(OH)_2$, in practice only have basic properties; for example, yellow $Cr(OH)_2$ reacts only with acids, forming blue aquo complexes:

$$Cr(OH)_2 + 2OH_3^+ + 2H_2O = [Cr(OH_2)_6]^{2+}$$

which is also the colour of the crystal hydrates, e.g. $Cr(ClO_4)_2 \cdot 6H_2O$, $CrSO_4 \cdot 5H_2O$, $CrCl_2 \cdot 4H_2O$, and $CrBr_2 \cdot 6H_2O$.

The dihalides quite easily absorb gaseous ammonia to form ammoniates, e.g. $[Cr(NH_3)_6]Cl_2$. Being strong reductants

$$Cr^{3+} + e^- = Cr^{2+}, \quad E^\circ = -0.41\ V$$

chromium(II) salts are easily oxidised in solution by atmospheric oxygen

$$4[Cr(OH_2)_6]^{2+} + O_2 + 4H^+ = 4[Cr(OH_2)_6]^{3+} + 2H_2O$$

while they can even reduce water, in the absence of an oxidant, decomposing it gradually with liberation of hydrogen:

$$2CrCl_2 + 2H_2O = 2Cr(OH)Cl_2 + H_2$$

Compounds of Cr(II) are obtained by reducing Cr(III) compounds, e.g. by nascent hydrogen in solution, or by heating in a hydrogen atmosphere. Dihalides can also be obtained by the interaction of the metal and gaseous HHal (at 600-700 °C).

There are few derivatives of Mo(II) and W(II); $EHal_2$ are the only binary compounds that have been studied (see below).

Cluster compounds. The *d* elements often form compounds containing groupings known as *clusters*, of two or more of their atoms linked

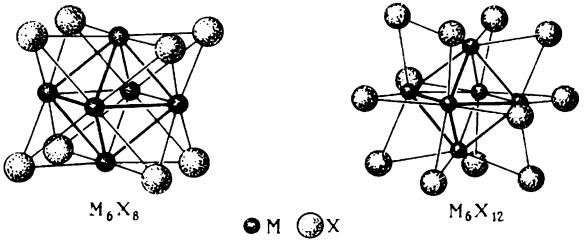
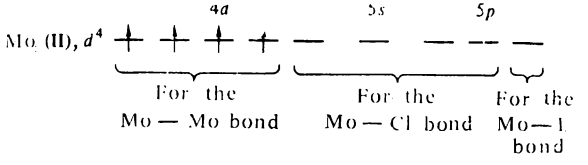


Fig. 229. Structure of the M_6X_8 type octahedral clusters (e.g. the $Mo_6Cl_8^{4+}$ ion) and M_6X_{12} type (e.g. the $Nb_6Cl_{12}^{2+}$ ion)

directly with one another. The cluster compounds so far known fall into two major classes: viz., (a) lower halides and oxides, and (b) polynuclear carbonyls.

The first type is formed mainly by Group V, VI, and VII 4*d* and 5*d* elements (Nb and Ta, Mo and W, Tc and Re). Di-, tri-, and hexanuclear clusters are distinguished among the halides and oxides. Yellow molybdenum dichloride $MoCl_2$ is an example of a *hexanuclear* (octahedral) cluster compound, whose formula, according to X-ray crystallography, is $[Mo_6Cl_8]Cl_4$. The $[Mo_6Cl_8]^{4+}$ complex is diamagnetic; its structure is shown in Fig. 229. Six molybdenum atoms are located at the centres of the cube's faces, forming an Mo_6 octahedron. Eight chlorines are at the apexes of the cube, each being linked with three molybdenum atoms. The chloride ions of the outer sphere act as bridges linking the $[Mo_6Cl_8]^{4+}$ clusters together.

To explain the structure of the complex we use purely qualitative concepts. Each Mo atom furnishes four electrons to form covalent Mo—Mo bonds with four neighbouring Mo atoms. Four free orbitals of each Mo atom are involved in the formation of Mo—Cl donor-acceptor bonds:



The $[Mo_6Cl_8]^{4+}$ cluster is stable and can pass unchanged from one compound to another. When an alkali acts on $MoCl_2$, for instance, a base $[Mo_6Cl_8](OH)_4$ is produced that reacts with acids to yield salts of this ion. The cluster $[Mo_6Cl_8]^{4+}$ can also act as a complexing agent to coordinate six ligands, one to each molybdenum atom, through the formation of $[Mo_6Cl_8L_6]$ complexes. Derivatives of the $[(Mo_6Cl_8)Cl_6]^{2-}$ ion and also the compound $[(Mo_6Cl_8)(OH)_4(OH_2)_2] \times$ $\times 12H_2O$, etc., have been obtained, for example. The structure of $MoBr_2$, WCl_2, and WBr_2 is similar to that of $MoCl_2$.

Groupings M_6C_{12} (Fig. 229) often occur among hexanuclear clusters. These have been found in $PtCl_2$ (Pt_6Cl_{12}), WCl_3 ($[W_6Cl_{12}]Cl_6$), Nb_6Cl_{14} ($[Nb_6Cl_{12}]Cl_2$), etc.

The halides of rhenium(III) and their derivatives are *triangular* clusters. The $ReCl_3$ crystal is build of Re_3Cl_9 groupings in which

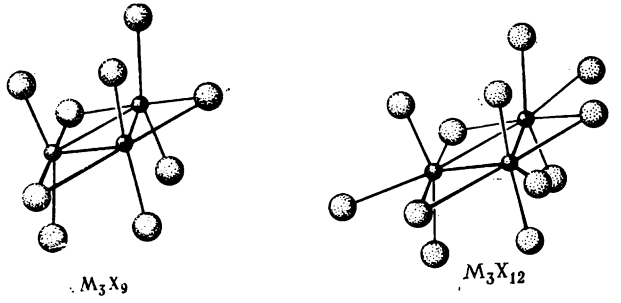


Fig. 230. Structure of triangular clusters of the M_3X_9 ($ReCl_3$) and M_3X_{12} ($CsReCl_4$) type

the rhenium atoms are joined in a triangle (Fig. 230). The internuclear distance d_{ReRe} here is 0.248 nm, which is 0.027 nm shorter than in the crystal of metallic rhenium ($d_{ReRe} = 0.275$ nm). Consequently the metal-metal bond is very strong here (presumably a multiplicity factor of two, Re=Re). The Re_3Cl_9 grouping is therefore very stable and remains unchanged when $ReCl_3$ is converted into a gas (up to 600 °C). When $ReCl_3$ reacts with concentrated hydrochloric acid, a trimeric $[Re_3Cl_{12}]^{3-}$ ion is formed (Fig. 230) with $d_{ReRe} = 0.248$ nm. Examples of the derivatives of $[Re_3Hal_{12}]^{3-}$ clusters are the red salts of $\overset{+1}{M}_3[Re_3Hal_{12}]$ type.

The *dinuclear* clusters include the $[Mo_2Cl_8]^{4-}$ and $[Re_2X_8]^{2-}$ ions, in which X is Cl, Br, or SCN. It has been established experimentally that the internuclear distance d_{ReRe} in the $[Re_2Cl_8]^{2-}$ ion (Fig. 231) is only 0.224 nm, i.e. 0.051 nm shorter than d_{ReRe} in the metal (0.275 nm). This extraordinarily short distance and the diamagnetism of this ion points to a quadruple Re≡Re bond (one σ bond, two π bonds, and one δ bond). A quadruple Mo≡Mo bond is similarly ex-

hibited in the diamagnetic $[Mo_2Cl_8]^{4-}$ ion, in which the internuclear distance d_{MoMo} is 0.214 nm (against the 0.278 nm in the metal).

If we take it that the z axis passes through the Re atoms, the bond arising can be explained as follows: one σ bond is formed by the

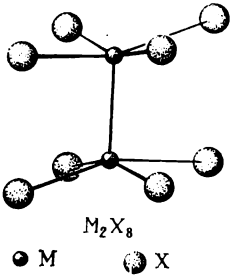
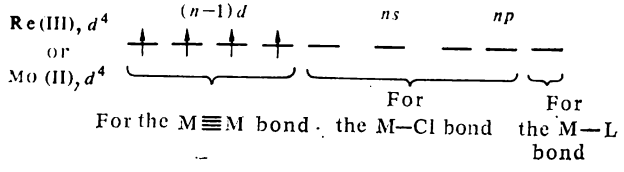


Fig. 231. Structure of a dinuclear cluster of M_2X_8 type (e.g. $K_2Re_2Cl_8 \times \times 2H_2O$)

overlapping of d_{z^2} orbitals, two π bonds are formed by the interaction of the d_{xz} and d_{yz} orbitals, and a δ bond by the overlapping of d_{xy} orbitals:



$M_2[Re_2Cl_8] \cdot 2H_2O$ can be considered a derivative of an $[Re_2Cl_8]^{2-}$ cluster.

MoO_2 is a dinuclear cluster oxide whose structure in the solid state is close to that of rutile (Fig. 70*b*); the internuclear distance $d_{MoMo} = 0.250$ and 0.310 nm (the shorter distance with a pair of interconnected molybdenum atoms). The compound is diamagnetic, which helps explain its structure. It has been found that there is an M_2 cluster of the dioxides, with a rutile structure, in WO_2, TcO_2, ReO_2, and VO_2.

Cluster compounds are typical of niobium and tantalum. Their halides have been best studied. Because of the specific character of their structure, their composition does not usually correspond to oxidation states expressed by whole numbers: for example

Composition	Cluster	Compounds
$EHal_{1.88}$ or E_6Hal_{11}	$E_6Hal_8^{3+}$	$[Nb_6I_8]I_3$
$EHal_{2.33}$ or E_6Hal_{14}	$E_6Hal_{12}^{2+}$	$[Nb_6Cl_{12}]Cl_2$, $[Ta_6Cl_{12}]Cl_2$, $[Ta_6Br_{12}]Br_2$, $[Ta_6I_{12}]I_2$
$EHal_{2.5}$ or E_6Hal_{15}	$E_6Hal_{12}^{3+}$	$[Nb_6F_{12}]F_3$, $[Ta_6Cl_{12}]Cl_3$, $[Ta_6Br_{12}]Br_3$
$EHal_{2.67}$ or E_3Hal_8	E_3Hal_8	Nb_3Cl_8, Nb_3Br_8, Nb_3I_8

The Nb and Ta atoms usually unite in octahedral and triangular groupings (see Figs. 229 and 230). Stable E_6Hal_{12} octahedral clusters have been found in crystal hydrates of the $Nb_6Cl_{14}\cdot 7H_2O$, $Nb_6Br_{14}\cdot 7H_2O$, and $Ta_6Cl_{14}\cdot 7H_2O$ type, which break up in solution into $[E_6Hal_{12}]^{2+}$ and $2Hal^-$ ions. Only two moles of the halide ions per mole of the compound are immediately precipitated from solution by the action of Ag^+ salts.

Halides of niobium and tantalum of variable composition, e.g. $NbCl_3$ — —$NbCl_{3.13}$, $TaCl_{2.9}$ —$TaCl_3$, etc., are also known.

The lower oxides of niobium and tantalum are also cluster compounds. Thus NbO consists of Nb_6O_{12} clusters. M—M bonds are also thought to be present in the lower oxyhalides $NbOI_2$ and $TaOCl_2$.

In cluster halides the *d* element atoms, irrespective of their oxidation state, furnish all their valence electrons for the construction of the M—M and M—Hal bonds (Tc and Re furnish seven, Mo and W six, and Nb and Ta five electrons). The tendency to use all their valence electrons in the formation of chemical bonds is thus realised in *4d* and *5d* elements through the formation of compounds in which they display their highest oxidation state or through the formation of cluster compounds.

The transition from metal to halide (or oxide) is consequently not necessarily connected with the breaking of all bonds between the metal atoms and their complete replacement by metal—halogen bonds. Many *d* element metals usually have high enthalpies of atomisation, i.e. high energy is needed to break the bonds between their atoms. The energy liberated during the formation of M—Hal bonds in lower halides of noncluster type is therefore not sufficient to compensate the energy spent on breaking all the M—M bonds.

Compounds of chromium(III), molybdenum(III) and tungsten (III). The most stable oxidation state of chromium is +3. The coordination number of chromium(III) is six, so that its complexes (unit cells) are octahedra. The valence electrons of its octahedral units are located in bonding and nonbonding orbitals only

$$[\sigma]^{12}\,[\pi_d^{\text{non}}]^3$$

The presence of three unpaired electrons accounts for the paramagnetic properties of Cr(III) derivatives. Most chromium(III) compounds are intensely coloured.

Chromium(III) *oxide* Cr_2O_3 is a dark green powder; in the crystalline state it is black with a metallic sheen. Its structure corresponds to an octahedral-tetrahedral coordination of the atoms (an α-Al_2O_3 type structure; see Fig. 72). It is refractory (m.p. 2265 °C) and inert, insoluble in water, acids, or alkalis. Its amphoteric nature is exhibited during fusion with corresponding compounds; when fused with

potassium disulphate, for instance, it forms chromium(III) sulphate

$$3K_2S_2O_7 = 3K_2SO_4 + 3SO_3$$
$$Cr_2O_3 + 3SO_3 = Cr_2(SO_4)_3$$

$$\underset{\text{Basic}}{Cr_2O_3} + 3K_2S_2O_7 = Cr_2(SO_4)_3 + 3K_2SO_4$$

but when fused with alkalis and their corresponding oxides, it forms oxychromates(III) known as *chromites*:

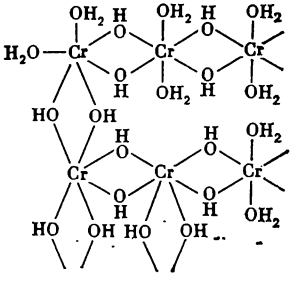
$$2KOH + \underset{\text{Acidic}}{Cr_2O_3} = 2KCrO_2 + H_2O$$

The oxychromates(III) of *d* elements, of the $\overset{+2}{M}(CrO_2)_2$ type, are coordinated polymers, i.e. *mixed* oxides of spinel type. The atoms of M(II) are present in their crystals in a tetrahedral configuration while the atoms of Cr(III) are in an octahedral one surrounded by oxygen atoms. Natural chromite $FeCr_2O_4$ is a mixed oxide of Cr(III) and Fe(II).

The greyish blue *hydroxide* $Cr(OH)_3$ precipitated from solution

$$Cr^{3+} + 3OH^- = Cr(OH)_3$$

has a variable composition $Cr_2O_3 \cdot nH_2O$. It is a polynuclear polymer with a layer structure, in which OH^- and OH_2 act as ligands, while the OH groups act as bridges



The composition and structure of $Cr_2O_3 \cdot nH_2O$ depend on the conditions in which it is produced. On standing, or in particular when heated, it changes its Cr—OH—Cr bonds for Cr—O—Cr ones and becomes unreactive. Fresh $Cr(OH)_3$ (i.e. $Cr_2O_3 \cdot nH_2O$) is readily soluble in the presence of acids and alkalis, which break the bonds in the layer polymer

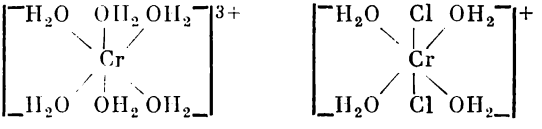
$$\underset{\text{Basic}}{Cr(OH)_3} + 3OH_3^+ = [Cr(OH_2)_6]^{3+}$$
$$\underset{\text{Acidic}}{Cr(OH)_3} + 3OH^- = [Cr(OH)_6]^{3-}$$

The preparation of chromium(III) hydroxide and its transition into cation $[Cr(OH_2)_6]^{3+}$ and anion $[Cr(OH)_6]^{3-}$ complexes can be expressed by the following summary equation

$$[Cr(OH_2)_6]^{3+} \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} Cr(OH)_3 \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} [Cr(OH)_6]^{3-}$$

The bluish violet $[Cr(OH_2)_6]^{3+}$ aquo complex is a component of certain crystal hydrates of Cr(III), e.g. of violet $CrCl_3 \cdot 6H_2O$, $CrBr_3 \cdot 6H_2O$, and $\overset{+1}{M}Cr(SO_4)_2 \cdot 12H_2O$ (alum). The findings of X-ray crystallography and the colour of the chromium alum point to an $[M(OH_2)_6][Cr(OH_2)_6](SO_4)_2$ structure. The alums are double salts formed by the interaction of solutions of $\overset{+1}{M}_2SO_4$ and $Cr_2(SO_4)_3$. Like certain other derivatives of Cr(III) they are used as mordants in the dyeing of textiles and in tanning leather.

The composition of cation aquo complexes varies, depending on the conditions (temperature, concentration, pH), and is accompanied with a change in their colour from violet to green, for example,



Blue-violet Dark green

The solid hexa-aquo crystal hydrate $CrCl_3 \cdot 6H_2O$, for example, has the following isomeric forms, depending on the orientation of the water molecules and the chloride ions

$[Cr(OH_2)_6]Cl_3$	$[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$	$[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$
Blue-violet	Pale green	Dark green

The isomerism due to dissimilar distribution of the water molecules and of outer-sphere ions between the inner and the outer spheres of complex compounds is called *hydrate*.

The existence of these isomers can be demonstrated by the following experiment. When $[Cr(OH_2)_6]Cl_3$ is dried over concentrated sulphuric acid in a desiccator, it does not lose water, $[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$ loses one mole, and $[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$ two moles of water per mole of the isomer. When silver nitrate $AgNO_3$ is added to their solutions, three, two and one moles of the chloride ion respectively are precipitated immediately. Further evidence of the correctness of the formulas can be obtained by measuring electrical conductivity: a

$[Cr(OH_2)_6]Cl_3$ solution has the highest level of conductivity, one of $[Cr(OH_2)_5Cl]Cl_2 \cdot H_2O$ is less conductive, while a solution of $[Cr(OH_2)_4Cl_2]Cl \cdot 2H_2O$ is least conductive, which fully agrees with the decreasing number of ions into which these compounds dissociate in equivalent molar concentrations.

Chromium trichloride $CrCl_3$ is reddish-violet. It is obtained by passing chlorine over hot metal or a red-hot mixture of Cr_2O_3 and charcoal:

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO$$

Anhydrous compounds, it should be noted, differ substantially in structure and properties from the corresponding crystal hydrates; $CrCl_3$, for example, is a polymer (layer structure, Fig. 232*a*), while

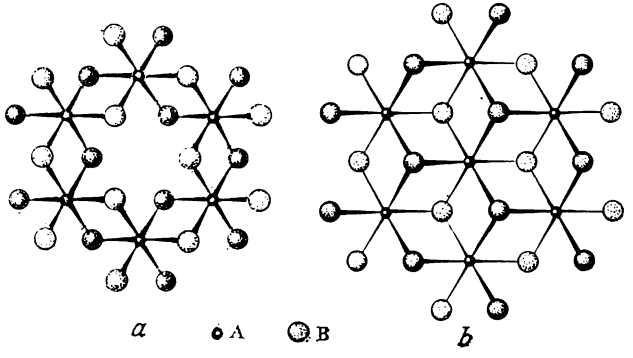


Fig. 232. Structure of a layer formed by octahedral AB_6 units of compounds (*a*) of the AB_3 and (*b*) of the AB_2 type

the crystal hydrate $CrCl_3 \cdot 6H_2O$ has an insular structure. Unlike $CrCl_3 \cdot 6H_2O$, $CrCl_3$ dissolves very slowly in water.

Pink $Cr_2(SO_4)_3$ is also poorly soluble in water, while the violet hydrate $Cr_2(SO_4)_3 \cdot 18H_2O$ is readily so.

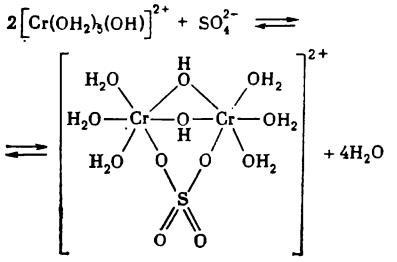
Compounds of Cr(III) are hydrolysed to a greater or lesser extent in solution. The formation of a hydroxypenta-aquo complex $[Cr(OH)(OH_2)_5]^{2+}$ can be regarded as the first step in the hydrolysis of the halides, sulphate, and nitrate of Cr(III):

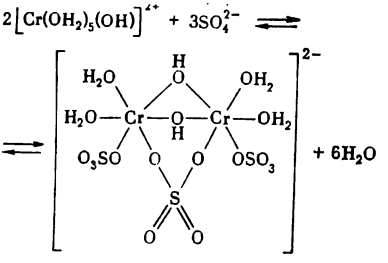
$$[Cr(OH_2)_6]^{3+} + H_2O \rightleftarrows [Cr(OH)(OH_2)_5]^{2+} + OH_3^+$$

$$Cr^{3+} + HOH \rightleftarrows CrOH^{2+} + H^+$$

These complexes can then be polymerised.

In the case of chromium sulphate, for example, the following products are obtained, depending on the temperature, pH, and concentration:





The violet solution here turns green.

Any attempt to precipitate Cr_2S_3 or $Cr_2(CO_3)_3$ by exchange reactions from an aqueous solution ends in precipitation of the hydroxide (because of hydrolysis):

$$2\overset{+3}{Cr} + 3CO_3^{2-} + 3H_2O = 2Cr(OH)_3 + 3CO_2$$

Apart from aquo complexes of Cr(III), violet cation amminocomplexes $[Cr(NH_3)_6]^{3+}$ are known. In the solid state the ammoniates are stable, but they gradually decompose in aqueous solutions

$$[Cr(NH_3)_6]Cl_3 + 3H_2O \rightleftarrows Cr(OH)_3 + 3NH_4Cl + 3H_3N$$

and are therefore most readily produced in nonaqueous solutions or in liquid ammonia.

The chromates(III) derivated from *anion* complexes of chromium(III) are most varied. The equations of the reactions by which they are obtained are as follows:

$$3KOH + Cr(OH)_3 = K_3[Cr(OH)_6]$$

Hexahydroxy chromate (III) (green)

$$\underset{\text{Basic compounds}}{3KCl} + \underset{\text{Acidic compounds}}{CrCl_3} = K_3[CrCl_6]$$

Hexachlorochromate (III) (pink-red)

$[Cr(OH)_6]^{3-}$ ions are emerald green. The hydroxychromates(III) are stable in the solid state, but in solutions only in the presence of excess alkali. They are decomposed in pure water. Other chromate(III) ions are more stable.

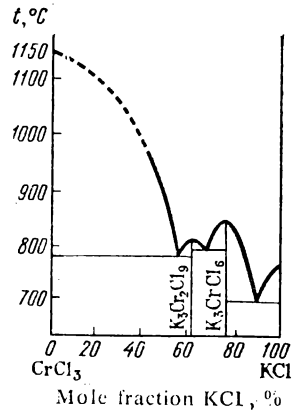
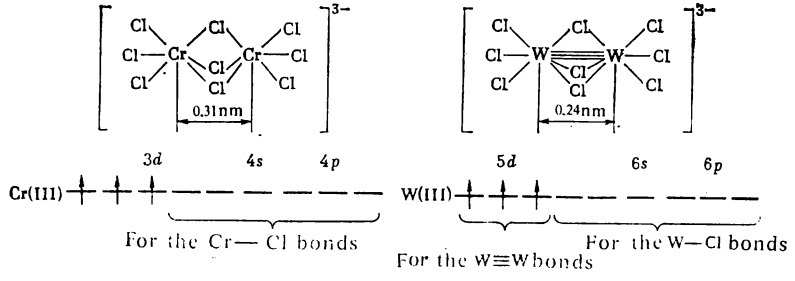


Fig. 233. Phase diagram of the $CrCl_3$—KCl system

Apart from the hexachlorochromates(III), complex chlorides with a $3KCl \cdot CrCl_3$ composition are known (see Fig. 233), derivatives of dinuclear $[Cr_2Cl_9]^{3-}$ complexes, whose structure corresponds to twin $CrCl_6$ octahedra with a common face (see Fig. 61*c*).

Research has shown that the $[Cr_2Cl_9]^{3-}$ ion is paramagnetic and has three unpaired electrons, while the similar $[W_2Cl_9]^{3-}$ ion is diamagnetic. The distance between the Cr atoms in $[Cr_2Cl_9]^{3-}$, moreover, is 0.07 nm longer than between the larger atoms of tungsten in $[W_2Cl_9]^{3-}$, which indicates that the $[W_2Cl_9]^{-3}$ ion is a cluster in contrast to $[Cr_2Cl_9]^{3-}$, and that a triple bond arises between the W atoms (one σ and two π bonds):



The internuclear distance d_{WW} in the $[W_2Cl_9]^{3-}$ ion is therefore much shorter (0.240 nm) than in metallic tungsten (0.280 nm).

Compounds of chromium(VI), molybdenum(VI) and tungsten(VI). An oxidation state of +6 is exhibited by chromium, molybdenum, and tungsten in their halides, oxyhalides, and oxides, and corresponding anion complexes:

$EHal_6$	$EOHal_4$	EO_2Hal_2	EO_3
—	—	$[CrO_3Hal]^-$	$[CrO_4]^{2-}$
$[MoF_7]^-$, $[WF_7]^-$	$[MoO_2Hal_4]^{2-}$	$[MoO_2F_3]^{3-}$	$[MoO_4]^{2-}$
$[MoF_8]^{2-}$, $[WF_8]^{2-}$	$[WO_2Hal_4]^{2-}$	$[WO_3F_3]^{3-}$	$[WO_4]^{2-}$

A coordination number of four is characteristic of chromium(VI), which corresponds to a tetrahedral structure of its anion complexes and unit cells. The coordination numbers of molybdenum(VI) and tungsten(VI) are more varied; four and six are relatively more stable.

In the Cr(VI)—Mo(VI)—W(VI) series there is a marked increase in the stability of similar derivatives. Comparison of the Gibbs' energies of formation provides further evidence of this:

	CrO_3 (c)	MoO_3 (c)	WO_3 (c)
ΔG_f°, kJ/mol	—506	—668	—764
	CrO_2Cl_2 (l)	MoO_2Cl_2 (l)	WO_2Cl_2 (c)
ΔG_f°, kJ/mol	—524	—623	—753
	CrO_4^{2-} (sol)	MoO_4^{2-} (sol)	WO_4^{2-} (sol)
ΔG_f°, kJ/mol	—730	—916	—920

The oxide CrO_3 and oxyhalides CrO_2Cl_2 and CrO_2F_2 are only stable for chromium(VI). Fluorides EF_6 (and also $MoCl_6$, WCl_6 and WBr_6), oxyhalides $EOHal_4$, and sulphides ES_3 are also characteristic of molybdenum(VI) and tungsten(VI).

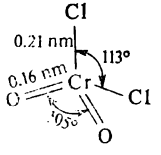
Chromium *hexafluoride* CrF_6 has not been well studied. It is a very unstable lemon-yellow powder. The hexafluorides of the analogues of chromium—MoF_6, a colourless liquid (m.p. 18 °C, b.p. 34 °C) and WF_6, a colourless gas (m.p. 2 °C, b.p. 17 °C)—are much more stable. They are formed by interaction of the simple substances. In contrast to SF_6 they are quite reactive and are easily decomposed, for example, in water with the formation of oxyhalides and HF. The acidic nature of EF_6 is also pronounced in their interaction with basic fluorides

$$EF_6 + KF = KEF_7$$

Oxyhalides CrO_2Hal_2 are more characteristic of chromium: brown-red CrO_2F_2 (m.p. 30 °C) and a red-brown CrO_2Cl_2 (f.p. —96.5 °C, b.p. 117 °C). The latter compound (*chromyl chloride*) is a liquid, formed by the interaction of dry CrO_3 and gaseous HCl:

$$CrO_3 + 2HCl = CrO_2Cl_2 + H_2O$$

EO_2Hal_2 molecules have a distorted tetrahedral structure with the E atom at the centre



Apart from EO_2Hal_2, oxyhalides with a composition $EOHal_4$ are also characteristic of molybdenum and tungsten. The oxyhalides of Mo(VI) and W(VI) are solids, usually volatile. The oxyhalides are acidic compounds with certain signs of amphoteric properties. In contrast to similar derivatives of sulphur SO_2Hal_2, the hydrolysis of EO_2Hal_2 is reversible:

$$EO_2Hal_2 + 2H_2O \rightleftharpoons H_2EO_4 + 2HHal$$

In the hydrolysis of CrO_2Cl_2 equilibrium is displaced to the right; MoO_2Cl_2 and WO_2Cl_2 are hydrolysed less, which indicates a weakening of acidic properties in the CrO_2Cl_2—MoO_2Cl_2—WO_2Cl_2 series.

Salts of the $\overset{+1}{M}[CrO_3Hal]$ type correspond to the chromium(VI) oxyhalides, and salts of the $\overset{+1}{M}_2[EO_2Hal_4]$ (where Hal = F and Cl) and $\overset{+1}{M}_3[EO_3F_3]$ types correspond to derivatives of molybdenum and tungsten. Trioxychlorochromates(VI) are orange crystalline solids. They can be obtained by the interaction of solutions of CrO_3 and basic chlorides:

$$KCl + CrO_3 = K[CrO_3Cl]$$

Trioxyhalogen chromates(VI) are gradually hydrolysed in water. The corresponding compounds of Mo(VI) and W(VI) are more stable.

The *trioxides* are crystalline solids: CrO_3 being dark red, MoO_3 white, and WO_3 yellow. MoO_3 has a layer lattice and WO_3 a coordination one (see Fig. 71) with octahedral EO_6 unit cells. CrO_3 has a chain structure formed by CrO_4 tetrahedra.

When heated, CrO_3 (m.p. 197 °C) quite readily decomposes liberating oxygen, but MoO_3 (m.p. 801 °C, b.p. 1155 °C) and WO_3 (m.p. 1473 °C, b.p. about 1670 °C) pass into the gaseous state without decomposition. Chromium trioxide is a strong oxidant reacting explosively with many oxidisable substances. CrO_3 is *poisonous*!

In contrast to MoO_3 and WO_3, chromium trioxide is easily soluble in water to form chromic acid, i.e. it is an acidic anhydride

$$H_2O + CrO_3 = H_2CrO_4$$

The acidic nature of MoO_3 and WO_3 is seen in their dissolution in alkalis:

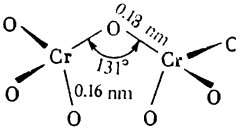
$$2KOH + EO_3 = K_2EO_4 + H_2O$$

Hydrogen tetraoxychromate(VI) H_2CrO_4 has not been isolated in the free state. Its aqueous solution is *chromic acid* ($K_{a1} = 1.6 \times 10^{-1}$, $K_{a2} = 3.2 \times 10^{-7}$).

The oxychromates(VI), oxymolybdates(VI) and oxytungstates(VI) of Group I *s* elements, and also Mg^{2+} and Ca^{2+}, are soluble in water. The CrO_4^{2-} ion is yellow, while the MoO_4^{2-} and WO_4^{2-} ions are colourless.

Many derivatives of polymeric oxyanions of very complicated composition and structure are known for Mo(VI) and W(VI). The capacity of the CrO_4^{2-} ion for polymerisation is less marked; nevertheless the following compounds, for example, are known: $K_2Cr_2O_7$

(dichromate), $K_2Cr_3O_{10}$ (trichromate), and $K_2Cr_4O_{13}$ (tetrachromate), all containing anions formed of CrO_4 tetrahedra linked in a chain. The structure of the $Cr_2O_7^{2-}$ ion is shown below:



Polychromates are formed by the action of acids on chromates. When an acid reacts with a strong solution of potassium chromate, for instance, the colour of the solution first becomes orange-red, then changes to darker shades through the formation of dichromates, and later of trichromates, etc.

$$2CrO_4^{2-} + 2H^+ = Cr_2O_7^{2-} + H_2O$$
$$3Cr_2O_7^{2-} + 2H^+ = 2Cr_3O_{10}^{2-} + H_2O, \text{ etc.}$$

When the solution is further acidified by concentrated sulphuric acid, dark red crystals of trioxide (chromic anhydride) are precipitated as it cools:

$$K_2CrO_4 + H_2SO_4 = CrO_3 + K_2SO_4 + H_2O$$

When polychromates are reacted with alkali, the reaction is reversed and the end product is the initial chromate. The reciprocal chromate-dichromate transition can be expressed by the equation of a reversible reaction:

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

Equilibrium is very mobile and can be shifted by altering the character of medium, through the precipitation of insoluble chromates of Ba^{2+}, Pb^{2+}, and Ag^+ whose solubility products are lower than those of the corresponding dichromates.

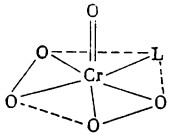
The most important oxychromates(VI) are salts of Na^+ and K^+, which are obtained by fusing Cr_2O_3 or chromite with the corresponding carbonates at 1000 °C to 1300 °C in air. Cr(III) is oxidised in this reaction to Cr(VI)

$$4Fe(\overset{+3}{Cr}O_2)_2 + 8Na_2CO_3 + 7O_2 = 8Na_2\overset{+6}{Cr}O_4 + 2Fe_2O_3 + 8CO_2$$

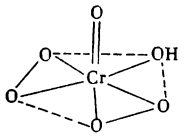
Sodium dichromate $Na_2Cr_2O_7 \cdot 2H_2O$ is obtained from acidified solutions of Na_2CrO_4. KCl precipitates a less soluble $K_2Cr_2O_7$ from a solution of $Na_2Cr_2O_7$ (Fig. 234).

Various *peroxy* complexes of chromium are known, for example, a blue $CrO(O_2)_2L$ (L = molecules of water or ether), and a violet complex, probably of a $[CrO(O_2)_2OH]^-$ composition. Both have the

configuration of a pentagonal pyramid with an oxygen atom at the apex



$[CrO(O_2)_2L]^-$



$[CrO(O_2)_2OH]^-$

The blue $CrO(O_2)_2L$ is formed by treating an acidic solution of the dichromate with hydrogen peroxide

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ + L = 2CrO(O_2)_2L + 5H_2O$$

$CrO(O_2)_2L$ is unstable in aqueous solution but is more stable in ether. It liberates oxygen during decomposition and turns into aquo complexes of Cr(III).

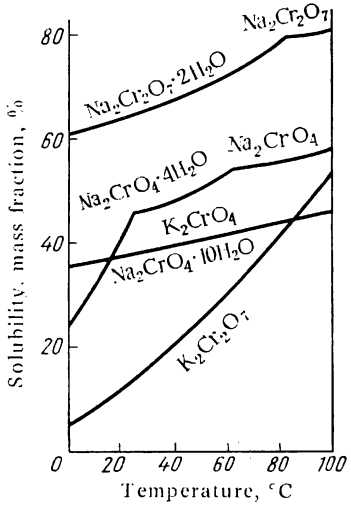


Fig. 234. Solubility of the chromates and dichromates of potassium and sodium

Derivatives of $[CrO(O_2)_2OH]^-$ are formed by the action of H_2O_2 on neutral solutions of dichromates:

$$K_2Cr_2O_7 + 6H_2O_2 = 2K[CrO(O_2)_2OH] + 5H_2O + O_2$$

Salts of type of $M^{+1}[CrO(O_2)_2OH]$ are explosive. Peroxy derivatives of Cr(V) and Cr(IV) are also known.

Sulphides ES_3, and also derivatives of the ions $[ES_4]^{2-}$, $[EOS_3]^{2-}$, $[EO_2S_2]^{2-}$, and $[EO_3S]^{2-}$, are known for molybdenum(VI) and tungsten(VI). They are obtained by passing hydrogen sulphide through solutions of molybdates and tungstates

$$K_2EO_4 + 4H_2S = K_2[ES_4] + 4H_2O$$

Chromium(VI) compounds are strong oxidants and are converted into derivatives of Cr(III) in redox reactions. In a neutral medium they yield chromium(III) hydroxide

$$Cr_2O_7^{2-} + 3(NH_4)_2S + H_2O = 2Cr(OH)_3 + 3S + 6H_3N + 2OH^-$$

in an acid medium derivatives of the cation complex $[Cr(OH_2)_6]^{3+}$

$$Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ = 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$$

and in an alkaline medium derivatives of the anion complex $[Cr(OH)_6]^{3-}$

$$2CrO_4^{2-} + 3(NH_4)_2S + 2OH^- + 2H_2O = 2[Cr(OH)_6]^{3-} + 3S + 6H_3N$$

The oxidising activity of oxychromates(VI) is highest in an acidic medium:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O, \quad E^0 = 1.33 \text{ V}$$

The oxidising ability of chromium(VI) compounds is used in chemical analysis and synthesis.

The oxidising properties of Mo(VI) and W(VI) compounds are exhibited only in interactions with the strongest reducing agents, e.g. with nascent hydrogen.

The most widely used derivatives of chromium and its analogues are compounds of chromium itself. Thus, Cr_2O_3 is used in making paints and as a catalyst. CrO_3 is used for obtaining chromium by electrolysis and chromium plating.

CHAPTER 6

Group VII *d* Elements

Manganese Mn, technetium Tc, and rhenium Re are full electron analogues with an $(n - 1)d^5ns^2$ configuration of the valence electrons, and form the manganese subgroup. Certain of their constants are as follows:

	$_{25}$Mn	$_{43}$Tc	$_{75}$Re
Atomic mass	54.9380	[99]	186.2
Valence electrons	$3d^54s^2$	$4d^55s^2$	$5d^56s^2$
Metallic atom radius, nm	0.130	0.136	0.137
Conventional ion E^{4+} radius, nm	0.052	—	0.072
Conventional ion E^{7+} radius, nm	0.046	0.056	0.056
Ionisation energy $E^0 \rightarrow E^+$, eV	7.44	7.28	7.88
Abundance, mole per cent	3.2×10^{-2}	traces	8.5×10^{-9}
Natural isotopes	^{55}Mn (100%)	—	^{185}Re (37.1%) ^{187}Re (62.9%)

As will be seen from the table, technetium and rhenium have similar atomic and ionic radii (because of lanthanide contraction) and are therefore closer to each other in their properties than to manganese.

The typical oxidation states of manganese are +2, +4, and +7, which corresponds to a stable nonbonding electron configuration d^5 or d^3, and also d^0. There are also compounds in which the oxidation state of manganese is 0, +3, +5, and +6. The highest oxidation state of technetium and rhenium +7 is their most stable one.

The most typical coordination numbers of manganese are six and four; technetium and rhenium also have coordination numbers of seven, eight, and even nine. The effect of the oxidation state and the

corresponding electron configuration of the atom on the structure of complexes (unit cells) of manganese and its analogues will be seen from Table 50.

Table 50. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of the Manganese Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical compounds
0	d^7	6	Octahedron	$E_2(CO)_{10}$
+2	d^5	4	Tetrahedron	$[MnCl_4]^{2-}$
		6	Octahedron	$[Mn(OH_2)_6]^{2+}$, $[MnF_6]^{4-}$, MnO, MnF_2, $MnCl_2$, $Mn(OH)_2$
+3	d^4	6	Octahedron	Mn_2O_3
+4	d^3	6	Octahedron	$[ECl_6]^{2-}$, MnO_2
+6	d^1	4	Tetrahedron	$[MnO_4]^{2-}$
		6	Octahedron	ReO_3, ReF_6
		8	Square antiprism	$[ReF_8]^{2-}$
+7	d^0	4	Tetrahedron	$[EO_4]^-$, E_2O_7
		6	Octahedron	$[ReO_3Cl_3]^{2-}$
		7	?	ReF_7
		8	Square antiprism	$K[ReF_8]$
		9		$[ReH_9]^{2-}$

The tendency of mangenese and its analogues to form anion complexes increases with the rise in oxidation state, while the tendency to form cation complexes decreases (i.e. the acidic character of their binary compounds increases).

Redox reactions are very typical of the chemistry of manganese. An acidic medium promotes the formation of cation complexes of Mn(II), and a strongly alkaline medium of anion complexes of Mn(VI). Derivatives of Mn(IV) (mostly MnO_2) are formed in oxidation-reduction processes in a neutral medium (and also in weakly acidic and alkaline media).

6.1. Manganese Subgroup

The main natural mineral of manganese is *pyrolusite* MnO_2. Rhenium very rarely forms independent minerals and only accompanies molybdenum in its minerals as a dispersed element (0.05-21 g/tonne). A rhenium mineral recently discovered and that is worth mentioning is *dzhezkazganite** $CuReS_4$. The existence of technetium (eka-man-

* From Dzhezkazgan, a town in the Kazakh SSR.

ganese) was predicted by Mendeleev. Technetium was the first element to be obtained artificially (hence its name). The most stable of the numerous isotopes of technetium is ^{99}Tc ($T_{1/2} = 2.2 \times 10^5$ years). Minute quantities of technetium are found in the Earth's crust. It is supposed that it is formed through the action of hard cosmic radiation on Mo, Nb, and Ru and through spontaneous fission of uranium nuclei.

The simple substances. The simple substances of manganese and its analogues are silvery-white metals. Four forms of manganese are known. The simple substances of the subgroup have the following physicochemical characteristics:

	Mn	Tc	Re
Density, g/cm³	7.44	11.49	21.04
M.p., °C	1245	2200	3180
B.p., °C	~ 2080	~ 4600	~ 5600
S°_{298}, J/K·mol	32.0	33.5	36.5
$\Delta H_{subl.,\ 298}$, kJ/mol	280	649	777
E°_{298} $E^{2+} + 2e^- = E$, V	—1.18	0.4	—
$EO_4^- + 8H^+ + 7e^- = E + 4H_2O$	—	0.47	0.37

Heats of sublimation (atomisation), and melting and boiling points increase in the Mn—Tc—Re series, probably because of the increasing proportion of covalent bonds formed by $(s - 1)d$ orbitals. Rhenium is second only to tungsten as regards refractoriness (m.p. 3380 °C).

The chemical activity of the simple substances falls in the Mn—Tc—Re series. Thus, Mn comes before hydrogen in the electromotive series, and Tc and Re after it. Mn reacts quite actively with dilute HCl and H_2SO_4, while Tc and Re react only with HNO_3. In accordance with their stable oxidation states, manganese reacts with dilute acids to form the cation aquo complex $[Mn(OH_2)_6]^{2+}$:

$$Mn + 2OH_3^+ + 4H_2O = [Mn(OH_2)_6]^{2+} + H_2$$

while technetium and rhenium yield an anion oxycomplex $[EO_4]^-$ in the reaction with nitric acid

$$3Tc + 7HNO_3 = 3HTcO_4 + 7NO + 2H_2O$$

Because of its high activity Mn is easily oxidised by oxygen, sulphur, and the halogens, especially when heated in powdered form. In the compacted state, it is stable in air since the oxide film that forms on its surface protects it against further oxidation. An even stronger oxide film is formed when manganese is acted upon by cold nitric acid. When technetium and rhenium are sufficiently heated they react with nonmetals; at 400 °C, for instance, Re burns in oxygen to give Re_2O_7.

Manganese is obtained by electrolysis of an aqueous solution of its sulphate and reduction of its oxides by silicothermy:

$$MnO_2 + Si = Mn + SiO_2$$

Rhenium is obtained, as a rule, by heating NH_4ReO_4 in a stream of hydrogen

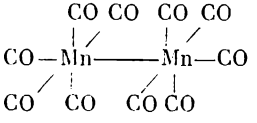
$$\overset{-3}{2}\overset{+1}{N}\overset{+7}{H_4}\overset{}{Re}\overset{}{O_4} + 4\overset{0}{H_2} = 2\overset{0}{Re} + \overset{0}{N_2} + 8\overset{+1}{H_2}O$$

Relatively large quantities of technetium are obtained from the fission products of uranium (wastes of the atomic industry).

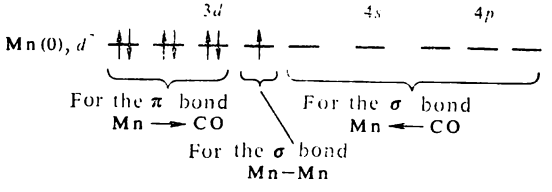
The bulk of manganese is smelted as *ferromanganese* (an alloy containing 60 to 90 per cent Mn and 40 to 10 per cent Fe) reducing a mixture of iron and manganese ores. About 90 per cent of the manganese produced is used in the steel industry for killing and alloying steels. It imparts corrosion resistance, ductility, and hardness to iron alloys. Technetium is corrosion-resistant and stable against the action of neutrons; for that reason it can be used for building nuclear reactors. Rhenium is mostly used in electrical engineering, and as a catalyst.

6.2. Compounds of the Manganese Subgroup Elements

Compounds of manganese(0), technetium(0), and rhenium(0). It has already been said that a zero oxidation state of *d* elements is exhibited in compounds with σ donor and π acceptor ligands. Carbonyls with a $E_2(CO)_{10}$ composition are known for manganese and its analogues:



They are diamagnetic, and a d^7 electron configuration may consequently be assigned to the atoms of manganese and its analogues in the zero oxidation state:



The M–CO chemical bond in metal carbonyls consists of sigma and pi bonds. The σ bond is formed through the donor-acceptor mechanism by free orbitals of the atom of *d* element and electron pairs

of the carbon atom of CO molecules. The π bond arises through the dative mechanism with involvement of free π* orbitals of CO and *d* electron pairs of the atom of the *d* element. Thus, Mn(0) attaches five CO molecules by five free $3d^4s^1p^3$ orbitals to form the $Mn(CO)_5$ radical. The Mn—CO bond is strengthened by the dative π interaction M → CO in which $3d_\varepsilon$ electron pairs of the manganese atom and π* orbitals of CO molecules are involved. A σ bond Mn—Mn is formed by unpaired electrons of manganese, so that the $Mn(CO)_5$ radicals are united in a $Mn_2(CO)_{10}$ molecule.

In ordinary conditions, yellow $Mn_2(CO)_{10}$ (m.p. 155 °C), colourless $Tc_2(CO)_{10}$ (m.p. 160 °C), and $Re_2(CO)_{10}$ (m.p. 177 °C) are easily sublimated solids.

Since the M—CO bond consists of σ and π bonds, more valence electrons of the *d* elements are needed for the formation of carbonyl clusters than for the formation of halide clusters in which the M—Hal bond is predominantly single. While halide clusters are then characteristic of *d* elements of Groups V, VI, and VII, carbonyl clusters are formed more often by *d* elements of Group VII (Mn, Tc, Re) and especially of Group VIII (Fe, Ru, and Os; Co, Rh and Ir). In other words, carbonyl clusters are typical of elements in which the number of valence electrons exceeds that required to form M → CO dative π bonds.

Metal carbonyls are capable of substitution and redox reactions. The CO groups in carbonyl molecules can thus be replaced by other ligands of the σ donor and π acceptor type (PF_3, PCl_3, NO, etc.), e.g. $Cr(PF_3)_3(CO)_3$.

The following are examples of the redox reactions:

$$\overset{0}{[Mn(CO)_5]_2} + 2Na = 2Na\overset{-1}{[Mn(CO)_5]}$$

$$\overset{0}{[Mn(CO)_5]_2} + Br_2 = 2\overset{+1}{Mn}(CO)_5Br$$

In the first $[Mn(CO)_5]_2$ is reduced and in the second oxidised, which corresponds to a change in the oxidation state of Mn from zero to −1 and +1, respectively.

The following extract from the periodic table shows the *d* elements that form neutral binary carbonyls and complexes containing (in addition to CO groups) atoms in the halogens (e.g. $Mn(CO)_5Br$)

Groups

V	VI	VII	VIII			I	II
V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Ta	W	Re	Os	Ir	Pt	Au	Hg

The solid line separates the symbol of the *d* elements that form binary carbonyls, while the broken line surrounds *d* elements that form carbonyl halides.

Other compounds of *d* elements in the zero oxidation state are also known, e.g. $Cr(PF_3)_6$, $Mo(PF_3)_6$, $Cr(PF_3)_3(CO)_3$, $Fe(NO)_4$, $Fe(NO)_2(CO)_2$ and $Ni[P(C_6H_5)_3]_4$. The molecule-ligands act in these compounds as σ donors and π acceptors of

electron pairs, the coordination numbers of the *d* elements also depend on the number of free orbitals arising during pairing of the complexing agents valence electrons.

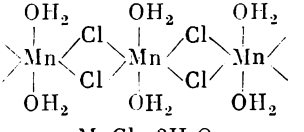
Compounds of manganese(II), technetium(II), and rhenium(II). The characteristic coordination number of manganese(II) is six, which corresponds to an octahedral arrangement of the bonds. Compounds of Mn(II) are paramagnetic and (except the cyanides) contain five unpaired electrons. The structure of high-spin octahedral complexes of Mn(II) corresponds to the following electron configuration

$$[\sigma_s]^2 [\sigma_p]^6 [\sigma_d]^4 [\pi_d^{non}]^3 [\sigma_d^*]^2$$

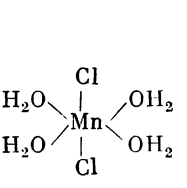
The binary compounds of Mn(II) are crystalline solids with a coordination or layer lattice. MnO and MnS, for example, have a NaCl type structure; MnF_2 has a rutile type structure (see Fig. 70*b*), and $MnCl_2$ and $Mn(OH)_2$, layer structures (Fig. 232*b*).

Most salts of Mn(II) are readily soluble in water; MnO, MnS, MnF_2, $Mn(OH)_2$, $MnCO_3$ and $Mn_3(PO_4)_2$ are barely soluble. When dissolved in water, salts of Mn(II) dissociate to form aquo complexes $[Mn(OH_2)_6]^{2+}$ which colour their solutions pink. The crystal hydrates of Mn(II), e.g. $Mn(NO_3)_2 \cdot 6H_2O$ and $Mn(ClO_4)_2 \cdot 6H_2O$ have the same colour.

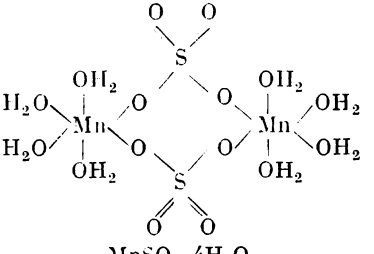
In crystal hydrates with fewer water molecules the role of ligands is played by the anion components of the substance (in addition to the OH_2 groups). In $MnCl_2 \cdot 2H_2O$ and $MnCl_2 \cdot 4H_2O$, for example, an octahedral structure arises around Mn(II) through the molecules of water and chlorine atoms; in the crystal hydrate $MnSO_4 \cdot 4H_2O$, the SO_4 group acts as the connecting bridge between the Mn(II) atoms:



$MnCl_2 \cdot 2H_2O$



$MnCl_2 \cdot 4H_2O$



$MnSO_4 \cdot 4H_2O$

The binary compounds of Mn(II) are amphoteric in their properties (with a preponderance of basic ones). In reactions without a change of oxidation state, they are characterised by a transition to cation complexes; the oxide MnO and the hydroxide $Mn(OH)_2$, for instance,

readily react with acids

$$MnO + 2OH_3^+ + 3H_2O = [Mn(OH_2)_6]^{2+}$$

but react with alkalis only after quite strong and prolonged heating

$$Mn(OH)_2 + 4OH^- = [Mn(OH)_6]^{4-}$$

Hydroxymanganates(II), $K_4[Mn(OH)_6]$, $Ba_2[Mn(OH)_6]$ (red), and certain others, have been isolated in the free state. They all completely dissociate in aqueous solutions, and for that reason neither metallic manganese nor its oxide or hydroxide react with alkali in ordinary conditions.

Manganese oxide MnO (a greyish-green substance, m.p. 1780 °C) has a variable composition ($MnO—MnO_{1.5}$) and semiconductor properties. It is usually produced by heating MnO_2 in an atmosphere of hydrogen, or by thermal decomposition of $MnCO_3$.

Since MnO does not react with water, $Mn(OH)_2$ (white) is obtained indirectly by the action of an alkali on a solution of an Mn(II) salt

$$MnSO_4\ (sol) + 2KOH\ (sol) = Mn(OH)_2\ (s) + K_2SO_4\ (sol)$$

Ammoniates of Mn(II), e.g. $[Mn(NH_3)_6]Cl_2$ and $[Mn(NH_3)_6](ClO_4)_2$ are also known. They easily decompose in water

$$[Mn(NH_3)_6]Cl_2 + 2H_2O \rightleftharpoons Mn(OH)_2 + 2NH_4Cl + 4H_3N$$

and can only exist in the solid state or in solutions with a great excess of ammonia and ammonium salts.

The acidic properties of Mn(II) compounds are displayed during their interaction with derivatives of alkali metals of the same type. Water-insoluble $Mn(CN)_2$ (white), for example, is dissolved in the presence of KCN, owing to complexation:

$$4KCN + Mn(CN)_2 = K_4[Mn(CN)_6]$$

Hexacyanomanganate(II)

The following reactions proceed in a similar way:

$$4KF + MnF_2 = K_4[MnF_6]$$

Hexafluomanganate(II)

$$2KCl + MnCl_2 = K_2[MnCl_4]$$

Tetrachloromanganate(II)

Most manganates(II) (except cyanide complexes) decompose in dilute solutions.

Manganates(II) often form crystal hydrates, e.g. $K_2[MnCl_4]\cdot 2H_2O$ and $K_2Mn(SO_4)_2\cdot 4H_2O$, which consist of octahedral complexes of the type of $[MnCl_4(OH_2)_2]^{2-}$ and $[Mn(SO_4)_2(OH_2)_4]^{2-}$.

Under the action of oxidants, derivatives of Mn(II) reveal reducing properties; thus $Mn(OH)_2$ is easily oxidised in an alkaline medium even by atmospheric molecular oxygen, and the precipitate $Mn(OH)_4$

obtained by an exchange reaction therefore soon darkens ($MnO_2 \cdot nH_2O$ is formed). In a strongly alkaline medium oxidation is accompanied with the formation of oxymanganates(VI), derivatives of the MnO_4^{2-} complex:

$$3\overset{+2}{Mn}SO_4 + 2K\overset{+5}{Cl}O_3 + 12KOH \xrightarrow[\text{fusion}]{} 3K_2\overset{+6}{Mn}O_4 + 2K\overset{-1}{Cl} + 3K_2SO_4 + 6H_2O$$

Strong oxidants like PbO_2 (which oxidises in an acidic medium) convert Mn(II) compounds into oxymanganates(VII), derivatives of the MnO_4^- complex:

$$2\overset{+2}{Mn}SO_4 + 5\overset{+4}{Pb}O_2 + 6HNO_3 = 2H\overset{+7}{Mn}O_4 + 3\overset{+2}{Pb}(NO_3)_2 + 2\overset{+2}{Pb}SO_4 + 2H_2O$$

This reaction is used in analytical chemistry to identify manganese compounds.

Compounds are not characteristic of Tc(II) and Re(II).

Compounds of manganese(IV), technetium(IV) and rhenium(IV). As we have seen, octahedral complexes with the electron configuration

$$[\sigma]^{12}[\pi_d^{\text{non}}]^3$$

are most characteristic of ions with a d^3 configuration. Thus the most characteristic coordination number for E(IV) is six. Examples of stable compounds of manganese(IV) are the dioxide MnO_2 and tetrafluoride MnF_4. Derivatives of hexahalogen manganate(IV) complexes of the type of MnF_6^{2-} and $MnCl_6^{2-}$ are also relatively stable while $MnCl_4$ is easily decomposed and MnF_4 is very reactive.

The *dioxide* MnO_2 is a blackish-brown solid, usually of a variable composition. It is the most stable manganese compound and is common in the Earth's crust (pyrolusite, etc.). Crystals of MnO_2 have a rutile type structure. In normal conditions MnO_2 does not dissolve in water and is quite inert (stable to the action of most acids when not heated).

Manganese dioxide is amphoteric in chemical nature. Black salt $Mn(SO_4)_2$ obtained by oxidising $MnSO_4$, is known; it is completely hydrolysed in water. When fused with alkalis or basic oxides, MnO_2 forms oxymanganates(IV) (known as *manganites*) of varied and complex composition:

$$MnO_2 + CaO = CaMnO_3$$

The simplest manganites are $\overset{+2}{M}MnO_3$ and $\overset{+1}{M}_4MnO_4$.

Compounds of Mn(IV) are strong oxidants:

$$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O, \quad E^\circ_{298} = 1.23 \text{ V}$$

When reacting with hot acids, MnO_2 does not form aquo complexes of Mn^{4+} but displays oxidising properties, oxidising concentrated

hydrochloric acid, for example:

$$\overset{+4}{Mn}O_2 + 4H\overset{-1}{Cl} = \overset{+2}{Mn}Cl_2 + \overset{0}{Cl}_2 + 2H_2O$$

When MnO_2 reacts with hot H_2SO_4 and HNO_3, it decomposes, liberating oxygen. It is a cheap oxidant widely employed in industry and the laboratory. In the glass industry it is used to decolour glass. It is also used in the manufacture of matches.

In the interaction of manganese(IV) compounds and the strongest oxidants, derivatives of Mn(VI) and Mn(VII) are produced,

$$3\overset{+4}{Mn}O_2 + K\overset{+5}{Cl}O_3 + 6KOH \xrightarrow[\text{fusion}]{} 3K_2\overset{+6}{Mn}O_4 + K\overset{-1}{Cl} + 3H_2O$$

$$2\overset{+4}{Mn}O_2 + 3\overset{+4}{Pb}O_2 + 6HNO_3 = 2H\overset{+7}{Mn}O_4 + 3\overset{+2}{Pb}(NO_3)_2 + 2H_2O$$

Compounds of the EO_2, $EHal_4$, $\overset{+1}{M}_2EO_3$, and $\overset{+1}{M}_2EHal_6$ type are known for Tc(IV) and Re(IV). The derivatives of Tc(IV) are relatively more stable than the similar compounds of Mn(IV) and Re(IV).

Compounds of manganese(VI), technetium(VI), and rhenium(VI). There are few compounds in which the oxidation state of manganese and its analogues is +6. Those of rhenium and technetium for which fluorides, chlorides, and several oxyhalides and oxides are known, are more stable: e.g.

ReF_6	$ReOF_4$	ReO_3
Pale yellow	Blue	Red
m.p. 19 °C	m.p. 108 °C	m.p. 160 °C
b.p. 34 °C	b.p. 172 °C	

The halides, oxyhalides, and oxides of Tc(VI) and Re(VI) are acidic compounds. Their corresponding anion complexes are

ReF_6	$ReOF_4$	ReO_3
$[ReF_8]^{2-}$	$[ReOF_5]^-$	$[ReO_4]^{2-}$

Liquid ReF_6 reacts with fluorides of the alkali metals to form salts of the ReF_8^{2-} ion

$$2KF + ReF_6 = K_2[ReF_8]$$

Derivatives of $[EOF_5]^-$ and $[EO_4]^{2-}$ are obtained indirectly.

The oxidation state +6 of manganese is slightly more stable in the MnO_4^{2-} anion, known as *manganate*. Derivatives of MnO_4^{2-}, TcO_4^{2-}, and ReO_4^{2-} (dark green) can only exist in aqueous solutions with a great excess of alkali; otherwise they undergo disproportionation:

$$3\overset{+6}{E}O_4^{2-} + 2H_2O = 2\overset{+7}{E}O_4^- + \overset{+4}{E}O_2 + 4OH^-$$

This process occurs particularly easily in an acidic medium, for that reason hydrogen derivatives of the H_2EO_4 type are not formed.

Disproportionation also accompanies the hydrolysis of halides and oxyhalides of Tc(VI) and Re(VI) (it is a quite vigorous process, yielding HEO_4, EO_2, and $HHal$). During the interaction of EO_3, $EOHal_4$, EF_6 and ECl_6 and alkalis, the corresponding salts and EO_2 are formed, e.g.

$$\overset{+6}{3}ECl_6 + 20KOH = 2K\overset{+7}{E}O_4 + \overset{+4}{E}O_2 + 18KCl + 10H_2O$$

Compounds of Mn(VI) are strong oxidants, especially in an acidic medium

$$MnO_4^{2-} + 4H^+ + 2e^- = MnO_2 + 2H_2O, \quad E^\circ_{298} = 2.26 \text{ V}$$

but under the action of stronger oxidants they are converted into oxymanganates(VII)

$$2K_2\overset{+6}{M}nO_4 + \overset{0}{Cl}_2 = 2K\overset{+7}{M}nO_4 + 2K\overset{-1}{Cl}$$

Derivatives of Tc(VI) and Re(VI), on the contrary, are readily oxidised by atmospheric molecular oxygen:

$$4K_2\overset{+6}{E}O_4 + O_2 + 2H_2O = 4K\overset{+7}{E}O_4 + 4KOH$$

Compounds of manganese (VII), technetium (VII), and rhenium (VII). The stability of the compounds increases in the Mn(VII)—Tc(VII)—Re(VII) series. Thus, only the oxide Mn_2O_7 and oxyfluoride MnO_3F are known for Mn(VII), while a whole range of compounds in the ReF_7—$ReOF_5$—ReO_2F_3—ReO_3F—Re_2O_7 series has been obtained for Re(VII). Some of these characteristics are as follows:

	MnO_3F	Mn_2O_7
	Dark green, m.p. 38 °C	Greenish-black, m.p. 5.9 °C

ReF_7	ReO_3F	Re_2O_7
Pale yellow, m.p. 48 °C	Yellow, m.p. 147 °C	Yellow, m.p. 296 °C

Stable tetrahedral anion complexes of the EO_4^- type correspond to manganese(VII), technetium(VII), and rhenium(VII). The maximum coordination number of rhenium is displayed in the compounds $K_2[ReF_9]$ and $K_2[ReH_9]$.

The increasing stability of similar compounds in the Mn(VII)—Tc(VII)—Re(VII) series is shown by the character of changes in enthalpy ΔH_f° and Gibbs' energy of formation ΔG_f°. The values of ΔG_f° and ΔH_f° for Tc(VII) and Re(VII) compounds are very close (because of lanthanide contraction) and are more negative than for similar compounds of Mn(VII), e.g.,

	Mn_2O_7 (c)	Tc_2O_7 (c)	Re_2O_7 (c)	MnO_4^- (sol)	TcO_4^- (sol)	ReO_4^- (sol)
$\Delta G^\circ_{f,\ 298}$, kJ/mol	—544	—938	—1098	—449	—630	—699

Manganese(VII) oxide Mn_2O_7 ($\Delta H_f^\circ = -743$ kJ/mol) is an unstable greenish-black, oily liquid, obtained by the action of concentrated sulphuric acid on manganates(VII):

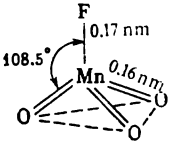
$$2KMnO_4 + H_2SO_4 = Mn_2O_7 + K_2SO_4 + H_2O$$

If special precautions are not taken, Mn_2O_7 decomposes and explodes:

$$2Mn_2O_7 = 4MnO_2 + 3O_2$$

The oxide of technetium(VII) Tc_2O_7 ($\Delta H_{f,298}^\circ = -1115$ kJ/mol) and of rhenium(VII) Re_2O_7 ($\Delta H_{f,298}^\circ = -1272$ kJ/mol) are stable yellow crystalline solids that can be obtained by direct oxidation of the simple substances.

In normal conditions MnO_3F is a liquid. Its molecule has the configuration of a distorted tetrahedron with the manganese atom at the centre ($\mu = 0.5 \times 10^{-29}$ C·m):



The molecules of ReO_3Hal and TcO_3Hal have similar structures.

The halides, oxyhalides, and oxides of E(VII) are typical acidic compounds that react vigorously with water to form acids:

$$E_2O_7 + H_2O = 2HEO_4$$
$$EO_3F + H_2O = HEO_4 + HF$$

Hydrogen tetraoxymanganate(VII) $HMnO_4$ has not been isolated in the free state; the maximum concentration of its aqueous solution is 20 per cent. Hydrogen tetraoxytechnate(VII) is a red crystalline substance; hydrogen tetraoxyrhenate(VII) $HReO_4$ has not been isolated. Aqueous solutions of HEO_4 are strong acids (*permanganic*, *pertechnic*, and *perrhenic* acid respectively). The strength of the acids diminish slightly in the $HMnO_4$—$HTcO_4$—$HReO_4$ series.

Most derivatives of MnO_4^-, TcO_4^-, and ReO_4^- (mistakenly still called *permanganates*, *pertechnates*, and *perrhenates*) are readily soluble in water. The salts of K^+, Rb^+, and Cs^+ are comparatively difficult to dissolve. The MnO_4^- ion is red-violet and TcO_4^- and ReO_4^- are colourless.

Compounds of manganese(VII) are strong oxidants. When Mn_2O_7 comes into contact with ether and alcohol, they ignite. Tetraoxyman

ganates(VII) are widely used in the laboratory as strong oxidants. The MnO_4^- ion can be reduced by the following reactions:

Medium		
acidic	$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$,	$E^0 = 1.58$ V
neutral and alkaline	$MnO_4^- + 2H_2O + 3e^- = MnO_2 + 4OH^-$,	$E^0 = 0.60$ V
strongly alkaline	$MnO_4^- + 1e^- = MnO_4^{2-}$,	$E^0 = 0.56$ V

Cation complexes of the $[Mn(OH_2)_6]^{2+}$ type are formed in an acidic medium, anion complexes of MnO_4^{2-} in a strongly alkaline medium, and derivatives of Mn(IV), usually MnO_2, in a neutral and alkaline medium.

Oxymanganates(VII) decomposes when heated

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

This reaction is used in the laboratory to obtain oxygen.

Our review shows that MnO_4^- ions are more stable than MnO_4^{2-} ones. In term of molecular orbital theory (see p 517), this can be explained as follows. The MnO_4^- ion contains 24 valence electrons, viz., seven electrons of the Mn atom ($3d^54s^2$), 16 electrons of the four O atoms ($2p^4$), and one electron from the charge of the ion. The MnO_4^{2-} ion, having a charge one unit greater, contains 25 electrons. The distribution of valence electrons between the molecular orbitals of the MnO_4^- and MnO_4^{2-} ions corresponds to the following electron configurations:

$$MnO_4^- \ [\sigma]^8 \ [\pi]^{10} \ [\pi^{non}]^6$$

$$MnO_4^{2-} \ [\sigma]^8 \ [\pi]^{10} \ [\pi^{non}]^6 \ [\pi^*]^1$$

As will be seen, one of the valence electrons in the second ion occupies an antibonding molecular orbital. For that reason, the MnO_4^{2-} ion is quite easily oxidised. The MnO_4^{3-} and MnO_4^{4-} ions are even less stable.

MnO_2 is the most commonly used compound of the manganese subgroup elements and is the initial product for obtaining all other manganese derivatives. It is also used as a catalyst, a cheap oxidant, a depolarising agent in galvanic cells, and so on.

CHAPTER 7

Group VIII *d* Elements

Group VIII of the periodic system comprises nine *d* elements, which form three subgroups, viz., the iron subgroup (iron Fe, ruthenium Ru, and osmium Os), the cobalt subgroup (cobalt Co, rhodium Rh, and iridium Ir) and the nickel subgroup (nickel Ni, palladium Pd, and platinum Pt).

As the $(n - 1)\,d$ orbitals are filled by a second electron the resemblance between neighbouring *d* elements in the period increases. Nickel, for example, is very much like Co and Fe (and like Cu). Furthermore, because of lanthanide contraction, a special similarity

of properties is observed in the Ru—Os, Rh—Ir, and Pd—Pt dyads. These elements of the fifth and sixth periods are often put into a family as the *platinum metals*.

7.1. Iron Subgroup

Iron Fe, ruthenium Ru, and osmium Os are the first *d* elements in their periods in which the *d* orbitals of the penultimate shell are filled by a second electron. They are therefore the originators of two subfamilies of *d* elements.

	$_{26}$Fe	$_{44}$Ru	$_{76}$Os
Atomic mass	55.847	101.07	190.2
Valence electrons	$3d^64s^2$	$4d^75s^1$	$5d^66s^2$
Metallic atom radius, nm	0.126	0.134	0.135
Conventional E^{2+} radius, nm	0.080	0.085	0.089
Conventional E^{3+} radius, nm	0.067	0.077	0.081
Conventional E^{4+} radius, nm	—	0.062	0.065
Conventional E^{8+} radius, nm	—	—	0.054
Ionisation energy $E^0 \rightarrow E^+$, eV	7.89	7.37	8.5
Abundance, mole per cent	2.0	1×10^{-7}	5×10^{-7}

Oxidation states +2 and +3 are most characteristic of iron, but derivatives in which its oxidation state is −2, 0, +4, and +6 are also known. The most stable compounds are Ru(IV) and Os(VIII).

Coordination numbers of six and four are characteristic of the elements of this subgroup. The effect of the oxidation state on the spatial configuration of molecules and complexes is shown in Table 51.

Table 51. **Oxidation States and Spatial Configuration of the Complexes (Unit Cells) of the Iron Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical compounds
−2		4	Tetrahedron	$[Fe(CO)_4]^{2-}$
0	d^8	5	Trigonal bipyramid	$E(CO)_5$, $Fe(PF_3)_5$
+2	d^6	4	Tetrahedron	$[FeCl_4]^{2-}$
		6	Octahedron	$[Fe(OH_2)_6]^{2+}$, $[E(NH_3)_6]^{2+}$, $[E(CN)_6]^{4-}$, FeO, $FeCl_2$
+3	d^5	4	Tetrahedron	$[FeCl_4]^-$, Fe(III) in Fe_3O_4
		6	Octahedron	$[Fe(OH_2)_6]^{3+}$, $[E(NH_3)_6]^{3+}$, $[E(CN)_6]^{3-}$, Fe_2O_3, FeF_3, $FeCl_3$
+4	d^4	6	Octahedron	$[RuCl_6]^{2-}$, $[OsCl_6]^{2-}$, RuO_2
+6	d^2	4	Tetrahedron	$[FeO_4]^{2-}$, $[RuO_4]^{2-}$
		6	Octahedron	RuF_6, OsF_6, $[OsO_2Cl_4]^{2-}$, $[OsO_2(OH)_4]^{2-}$, $[OsNCl_5]^{2-}$
+8	d^0	4	Tetrahedron	RuO_4, OsO_4, $[OsO_3N]^-$
		6	Octahedron	$[OsO_3F_3]^-$, $[OsO_4(OH)_2]^{2-}$

Iron is one of the commonest elements in the Earth's crust (see Table 25). It is a constituent of many minerals that form deposits of iron ores. The most important ores are *brown haematites* (main mineral *hydrogoethite* $HFeO_2 \cdot nH_2O$), *red iron ore* (main mineral *haematite* Fe_2O_3), *magnetic iron ores* (main mineral *magnetite* Fe_3O_4), and *siderite ores* (main mineral *siderite* $FeCO_3$). Iron is contained in natural waters. Native iron occurs occasionally either of cosmic (meteorite) or terrestrial origin. Meteorite iron usually contains considerable admixtures of cobalt and nickel. Iron is a constituent of haemoglobin.

Ruthenium and osmium occur together with Pt and Pd in polymetallic ores, and as native alloys with irridium and platinum.

The simple substances. Iron and ruthenium are silvery white metals, while osmium is bluish white. Osmium is the heaviest of all the metals, and very hard, but submits to grinding to powder.

	Fe	Ru	Os
Density, g/cm³	7.87	12.4	22.5
M.p., °C	1539	2300	2800
B.p., °C	2880	~ 3700	~ 4200
Electrical conductivity	10	10	11
$\Delta H^\circ_{subl.,\,298}$, kJ/mol	418	603	670
S°_{298}, J/K·mol	27.15	28.5	32.6

In accordance with the increasing proportion of covalent bonds (through 3*d*, 4*d*, and 5*d* electrons respectively), the heat of sublimation, melting point, and boiling point rise markedly in the Fe—Ru—Os series.

Iron has four allotropic forms (Fig. 235). At temperatures under 770 °C, α-Fe, which has a body-centred cubic lattice and ferromagnetic properties, is stable. At 770 °C it is converted into β-Fe, its ferromagnetic properties disappear,

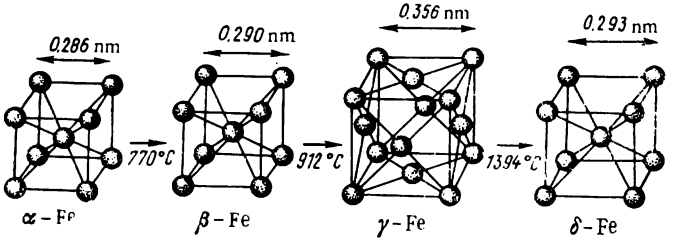


Fig. 235. The polymorphic transformation of iron

and the metal becomes paramagnetic, although the crystal structure does not alter substantially. At 912 °C polymorphic transformations occur in which the body centred cubic structure becomes face-centred (γ-Fe), the metal remaining paramagnetic. At 1394 °C, a new polymorphic transformation takes place and δ-Fe is formed with a body-centred cubic lattice that remains stable up to the melting point of iron (1539 °C). Ruthenium and osmium have hexagonal crystal lattices.

Iron is a metal of medium chemical activity. In the absence of moisture it is passivated in normal conditions, but in damp air it is readily oxidised and becomes coated with rust. When heated (especially in a finely divided state) it reacts with almost all nonmetals to form (depending on the conditions and the activity of the nonmetal) solid solutions (with C, Si, N, B, P, H), metal-like compounds (Fe_3C, Fe_3Si, Fe_3P, Fe_4N, Fe_2N) or salts and salt-like compounds (FeF_3, $FeCl_3$, FeS). Iron is oxidised by oxygen to form oxides of a non-stoichiometric composition.

Iron readily reacts with dilute acids in the absence of oxygen to form derivatives of Fe(II): $Fe^{2+} + 2e^- = Fe$, $E^\circ_{298} = -0.44$ V. In concentrated HNO_3 and H_2SO_4 it is passivated. In normal conditions it is insoluble in alkalis.

Ruthenium and osmium (like the simple substances of most other *d* elements of the fifth and sixth periods) are chemically inactive. In normal conditions, even the most active non-metals have no effect on the compact metals, but finely divided osmium is gradually oxidised to OsO_4 by oxygen and concentrated HNO_3. Ruthenium is oxidised very slowly by oxygen, and only at temperatures above 450 °C, yielding RuO_2 (volatile RuO_4 at higher temperatures).

As compact metals, ruthenium and (to a lesser extent) osmium are stable in acids and their mixtures, but are readily decomposed in solutions of hypochlorites and when fused with alkalis in the presence of oxidants, i.e. in conditions promoting the formation of oxyanions with high oxidation states of the *d* elements

$$\overset{0}{E} + 3KClO_3 + 2NaOH = Na_2\overset{+6}{E}O_4 + 3KCl + H_2O$$

Because of their great hardness and high resistance to corrosion, osmium and its alloys with ruthenium (and iridium) are used for making important parts of measuring instruments and tipping the nibs of fountain pens. Osmium, ruthenium, and iron are highly effective catalysts for the synthesis of ammonia (see Fig. 155); ruthenium and osmium are effective catalysts of hydrogenation, and the synthesis of long-chain hydrocarbons.

7.2. Compounds of the Iron Subgroup Elements

Metallic and metal-like compounds. Like other *d* elements, iron forms compounds of a metallic type with low-activity nonmetals. With carbon it yields the carbide Fe_3C (*cementite*), solid solutions (*austenite*, a solution of carbon in gamma iron; and *ferrite*, a solution of carbon in alpha iron), and eutectic mixtures (iron and carbon, cementite and austenite, iron and cementite, etc.). Study of the conditions in which iron forms compounds with carbon is very important for understanding the structure, composition, and properties of ferroalloys. Depending on the crystallisation conditions and the

composition of the Fe—C melt, the structure and the ratio of the constituents vary substantially, and consequently, also, the physicochemical properties of the alloys obtained. Ferro-alloys containing under 2 per cent of C are known as *steels*; those containing 2 to 4 per cent C are called *cast* or *pig iron*, and those with less than 0.3 per cent C, *mild* or *low-carbon steels* (*soft iron*).

The properties of steels are also greatly affected by their thermal treatment, which induces secondary changes in the ratios of the compounds and the structure of the alloys. During the slow cooling (*tempering*) of steel, for example, austenite gradually decomposes into cementite and ferrite, and the steel becomes mild, but when it is cooled (*quenched*) quickly, the austenite is converted into *martensite* (a supersaturated solid solution of C in alpha iron) and the steel acquires great hardness and a certain brittleness.

The physicochemical properties of ferroalloys are altered even more when alloying components, are added, e.g. Cr, Mn, Ni, Co, Ti, W, Mo, Cu, Si, B, V, Zr. The alloying elements interact with the iron and carbon (and their compounds) to form new metallic and metal-like compounds. As a result, the whole complex of the mechanical and physicochemical properties of the steel is altered.

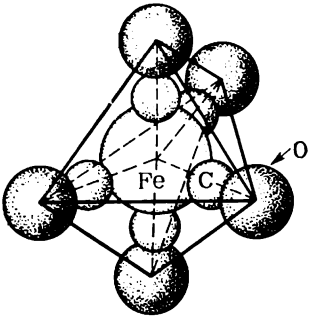


Fig. 236. Structure of the molecule of iron pentacarbonyl $Fe(CO)_5$

Pig iron is prepared by reducing iron ores in blast furnaces. The reduction of the ore can be expressed by the following equation:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2$$

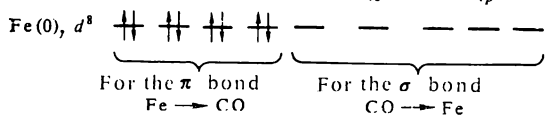
Subsequent treatment of the pig iron (by the Bessemer and open hearth processes, vacuum smelting in electric furnaces, etc.) yields steel and iron. The conversion of pig iron into steel consists in removing excess carbon and deleterious impurities (sulphur, phosphorus) by oxidation (burning out) during smelting. Pure iron is obtained by electrolysis of solutions of its salts or by thermal decomposition of certain compounds.

Compounds of iron(0), ruthenium(0) and osmium(0). Like the elements of the manganese and chromium subgroups, iron and its analogues can form compounds only through a donor-acceptor interaction. Thus heating of powdered iron in a current of CO at between 150 °C and 200 °C and a pressure around 1×10^7 to 2×10^7 Pa yields iron pentacarbonyl $Fe(CO)_5$

$$Fe + 5CO = Fe(CO)_5$$

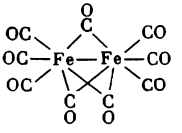
which is a volatile, yellow liquid (f.p. —20 °C, b.p. 103 °C), soluble in benzene and ether but insoluble in water. Its molecule has the configuration of a trigonal bipyramid (Fig. 236), i.e. corresponds to

dsp^3 hybridisation of the σ bonding orbitals of iron:



The molecules of the pentacarbonyls of ruthenium $Ru(CO)_5$ (f.p. −22 °C) and osmium $Os(CO)_5$ (f.p. −15 °C), which are colourless liquids in normal conditions, have a similar structure.

Carbonyls of iron and its analogues of more complicated structure have also been obtained. When $Fe(CO)_5$ is irradiated with ultraviolet rays, CO is formed and the initial substance turns into dark yellow crystals of enneacarbonyl $Fe_2(CO)_9$ (m.p. 100 °C). This is a cluster-type dinuclear compound in which the iron atoms are linked directly and through CO bridges:



Trinuclear dodecacarbonyls $E_3(CO)_{12}$ are also known. In normal conditions they are green solids $Fe_3(CO)_{12}$ (decomposes at 100 °C) and $Ru_3(CO)_{12}$, and yellow $Os_3(CO)_{12}$ (m.p. 224 °C).

The carbonyls break down when heated, which is employed to refine metals of the highest purity. The process of obtaining $Fe(CO)_5$ and its decomposition can be shown as follows:

$$\text{Fe (impure)} + 5\text{CO} \xrightarrow[1\times10^7-2\times10^7\text{Pa}]{180\ ^\circ\text{C}-220\ ^\circ\text{C}} \text{Fe(CO)}_5 \xrightarrow{230\ ^\circ\text{C}-330\ ^\circ\text{C}} \text{Fe (pure)} + 5\text{CO}$$

In the first stage of the process, CO reacts selectively with iron-containing material to yield $Fe(CO)_5$. Purification from microadmixtures of other metals takes place then. In the second stage, thermal decomposition of the carbonyl yields pure iron and CO which can be reused in the process.

The carbonyls of metals are oxidised and reduced with partial or complete preservation of the coordinated CO groups. Thus $Fe(CO)_5$ reacts with metallic sodium in liquid ammonia

$$\overset{0}{\text{Fe}}(\text{CO})_5 + 2\text{Na} = \text{Na}_2[\overset{-2}{\text{Fe}}(\text{CO})_4] + \text{CO}$$

and with alkali in an alcoholic solution

$$\text{Fe(CO)}_5 + 4\text{KOH} = \text{K}_2[\text{Fe(CO)}_4] + \text{K}_2\text{CO}_3 + 2\text{H}_2\text{O}$$

Compounds of the $M_2^{+1}[Fe(CO)_4]$ type are salts. They are readily hydrolysed forming hydrocarbonyl (carbonyl hydrate) $H_2Fe(CO)_4$. The $[Fe(CO)_4]^{2-}$ ion can be regarded as a derivative of iron in a −2 oxidation state, and the $[Fe_2(CO)_8]^{2-}$

ion of iron in a −1 oxidation state. $H_2Ru(CO)_4$ and $H_2Os(CO)_4$ are also known. Derivatives of the type of $\overset{+2}{M}Fe(CO)_4$ (where $\overset{+2}{M}$ is a *d* element) are mixed carbonyls of two metals.

When $Fe(CO)_5$ is carefully oxidised with halogens, one of CO groups is replaced by two halogen atoms

$$\overset{0}{Fe}(CO)_5 + I_2 = [\overset{+2}{Fe}(CO)_4]I_2 + CO$$

Nitrosyls $E(NO)_4$ and nitrosyl-carbonyls $E(CO)_2(NO)_2$, and compounds of the type of $Fe(NO)_2(PF_3)_2$, etc., are also known for Fe(0), Ru(0), and Os(0).

Compounds of iron(II), ruthenium(II) and osmium(II). A coordination number of six is most typical of Fe(II), which corresponds to an octahedral arrangement of the bonds in its complexes and unit cells (Table 51); it has this coordination number, for example, in crystals of FeO (structure of the NaCl type), FeF_2 (rutile structure), and $FeCl_2$ (layer structure of the type shown in Fig. 232*b*) and in many complex ions, e.g. $[Fe(OH_2)_6]^{2+}$, $[FeF_6]^{4-}$, $[Fe(CN)_6]^{4-}$, etc. There are also tetrahedral complexes of the type of $FeCl_4^{2-}$ and $Fe(CNS)_4^{2-}$.

Pale green cation aquo complexes of $[Fe(OH_2)_6]^{2+}$ exist in aqueous solutions. Hexa-aquo complexes are formed when Fe(II) salts are dissolved in water or during the interaction of iron, its black oxide FeO, white hydroxide $Fe(OH)_2$, black sulphide FeS, white carbonate $FeCO_3$ and dilute acids, e.g.

$$FeO + 2OH_3^+ + 3H_2O = [Fe(OH_2)_6]^{2+}$$

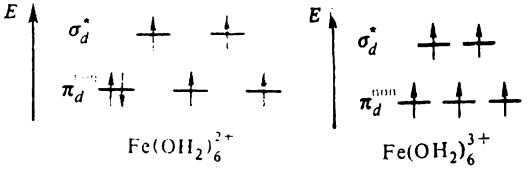
$$FeCO_3 + 2OH_3^+ + 3H_2O = [Fe(OH_2)_6]^{2+} + CO_2$$

Iron(II) forms salts with almost all anions. When aqueous solutions are evaporated, green crystal hydrates are usually precipitated, e.g. $Fe(ClO_4)_2 \cdot 6H_2O$, $Fe(NO_3)_2 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $FeBr_2 \cdot 6H_2O$, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (*Mohr's salt*).

Like most other complexes of Fe(II), the aquo ion $[Fe(OH_2)_6]^{2+}$ is paramagnetic, which corresponds to the following electron configuration

$$[\sigma]^{12}[\pi_d^{non}]^4[\sigma^*_{x^2-y^2}]^1[\sigma^*_{z^2}]^1$$

Because of its loss of one π_d^{non} electron, the ion $[Fe(OH_2)_6]^{2+}$ is quite easily oxidised to $[Fe(OH_2)_6]^{3+}$:



The standard potential of the system $Fe^{3+} + e^- = Fe^{2+}$ is 0.77 V; the Fe^{2+} ion can therefore be oxidised in an acidic medium even by

molecular oxygen

$$2Fe^{2+} + 1/2O_2 + 2H^+ = 2Fe^{3+} + H_2O, \quad E^0 = 0.46 \text{ V}$$

In the presence of moisture solid $FeCO_3$ and FeS are oxidised by atmospheric oxygen, e.g.

$$4FeS + O_2 + 10H_2O = 4Fe(OH)_3 + 4H_2S$$

Oxidation becomes specially easy in an alkaline medium; $Fe(OH)_2$, for instance, begins to be converted into $Fe(OH)_3$ as soon as it is formed. The white precipitate therefore soon darkens:

$$4Fe(OH)_2 + O_2 + 2H_2O = 4Fe(OH)_3$$

In analytical practice Fe^{2+} is determined by the following reactions:

$$5[Fe(OH_2)_6]^{2+} + MnO_4^- + 8OH_3^+ = 5[Fe(OH_2)_6]^{3+} + [Mn(OH_2)_6]^{2+} + 6H_2O$$

or

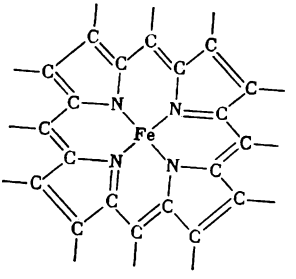
$$5Fe^{2+} + MnO_4^- + 8H^+ = 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Cation ammino complexes of Fe(II), e.g. ammino complexes of $[Fe(NH_3)_6]^{2+}$, are also known. The ammoniates are formed by the interaction of ammonia and anhydrous compounds of iron(II), e.g. its halides. Ammoniates are only stable in the solid state and in saturated aqueous solutions of ammonia. The ammoniates of Fe(II) are easily decomposed in water:

$$[Fe(NH_3)_6]Cl_2 + 2H_2O \rightleftharpoons Fe(OH)_2 + 2NH_4Cl + 4H_3N$$

Chelate ammino complexes are much more stable in solutions.

The most important chelate complexes of iron(II) are the *haems*:



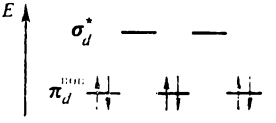
Haems form part of *haemoglobin*, which performs the function of oxygen transporter in the organism. The active centre in the process of combining oxygen is the iron(II) atom of haem. The process is reversible: in the lungs, where the partial pressure of oxygen is high, the O_2 molecule combines with the iron atom, while in the tissues, where the oxygen pressure is low, oxygen is liberated.

Most of the derivatives of anion complexes of Fe(II), *ferrates*(II), are unstable and resemble double salts. They include, e.g. $\overset{+1}{M}_2[FeCl_4]$ and $\overset{+1}{M}_2[Fe(CNS)_4]$. When boiled in concentrated alkalis (in a reducing atmosphere) $Fe(OH)_2$ forms hexahydroxyferrates(II), e.g. green $Na_4[Fe(OH)_6]$ and $Ba_2[Fe(OH)_6]$, which are completely hydrolysed in water.

The cyanide complex of Fe(II) $[Fe(CN)_6]^{4-}$ ($K_{st} = 8 \times 10^{36}$) is most stable and is easily produced

$$6KCN + FeSO_4 = K_4[Fe(CN)_6] + K_2SO_4$$

This ion is diamagnetic: $[\sigma]^{12}\ [\pi_d^{non}]^6$



The formation of the cyanide complexes is explained in the same way as that of carbonyl complexes (see Fig. 228). All the valence electrons and orbitals of the *d* element are involved in the formation of bonds (through donor-acceptor and dative mechanisms). The distribution of valence electrons in the $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ ions, for example, is similar to that in the isoelectronic molecule $Cr(CO)_6$ (see p. 552).

Owing to the superimposition of the σ and π compounds, the M ⟵ CN bond is very strong and cyanide complexes have high stability constant

	$[Fe(CN)_6]^{4-}$	$[Ag(CN)_2]^-$	$[Ni(CN)_4]^{2-}$	$[Hg(CN)_4]^{2-}$
K_{st}	8×10^{36}	7×10^{19}	1×10^{31}	4×10^{40}

These values are much higher (several orders) than those for the corresponding ammoniates, fluoride and other complexes, for example:

	FeF_3^{3-}	$Ag(NH_3)_2^+$	$Ni(NH_3)_6^{2+}$	$Fe(CNS)_4^-$
K_{st}	1.26×10^{16}	1.74×10^{7}	1.02×10^{8}	3.39×10^{1}

The cyanide ion is negatively charged and so is a poor π acceptor. The cyanide complexes of metals are less stable in their low oxidation states than the corresponding carbonyl derivatives. On the other hand, because of the charge, the CN^- ion is a stronger σ donor than CO and so forms relatively stable derivatives with metals with high oxidation states, for example, $[\overset{+4}{Mo}(CN)_8]^{4-}$.

The interaction of hexacyanoferrates(II) and strong acids yields $H_4[Fe(CN)_6]$, a white, fine, crystalline, diamagnetic powder that is readily soluble in water and is a quite strong (ferrocyanic) acid.

The most widely used cyanoferrate(II) is potassium ferrocyanide $K_4[Fe(CN)_6]\cdot3H_2O$ (*yellow prussiate of potash*). Potassium hexacyanoferrate(II) used to be obtained by fusing slaughter house wastes with iron filings and potassium carbonate. It is now obtained from cyanides that are by-products of the dry distillation of coals.

The hexacyanoferrates(II) of *d* elements, e.g. $Cu_2[Fe(CN)_6]$ and $Fe_2[Fe(CN)_6]$ have a coordination structure. The Fe atoms and the atoms of the *d* element concerned are connected in their crystals via CN groups, so that they are *mixed* cyanides. Most of them are intensely coloured and poorly soluble in water.

Potassium ferrocyanide is widely used in analytical chemistry to identify Fe^{3+} ions

$$FeCl_3 + K_4[Fe(CN)_6] = KFe[Fe(CN)_6] + 3KCl$$

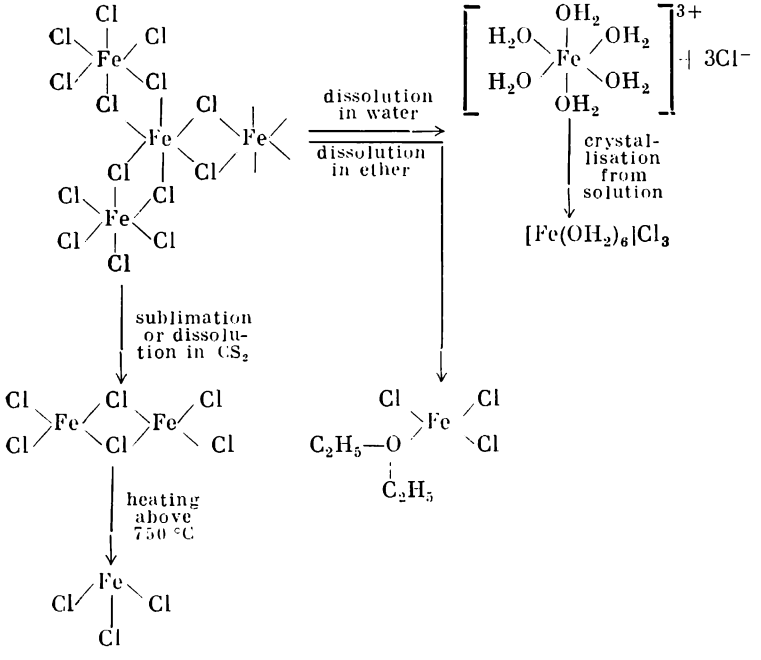
or

$$Fe^{3+} + K^+ + [Fe(CN)_6]^{4-} = \overset{+3\ +2}{KFe[Fe(CN)_6]}$$

An intensely blue, barely soluble mixed cyanoferrate(II) of potassium (I) and iron(III) is formed in this reaction, the compound known as *Prussian (Berlin) blue.*

The most stable derivatives of ruthenium(II) and osmium(II) are complex cyanides of the type of $\overset{+1}{M}_4[E(CN)_6]$.

Compounds of iron(III), ruthenium(III), and osmium(III). The coordination numbers of Fe(III) are six and four, which correspond to tetrahedral and octahedral arrangements of the bonds. Iron thus has a coordination number of six in crystalline $FeCl_3$. As this compound dissolves in water, octahedral $[Fe(OH_2)_6]^{3+}$ complexes are formed. In nonpolar solvents (e.g. CS_2), and during sublimation, Fe_2Cl_6 molecules (of the type of Al_2Cl_6) are produced:



Unlike layer $FeCl_3$ (m.p. 308 °C, b.p. 315 °C), ferric trifluoride FeF_3 has a coordination lattice of the ReO_3 type, is high-melting (sublimes at 1000 °C), insoluble in water, and chemically inactive.

The *oxide* Fe_2O_3 (from dark red to black) exists in three forms, similar in structure to Al_2O_3. Crystals of α-Fe_2O_3 (*haematite*), like corundum, have an octahedro-tetrahedral coordination of atoms (see Fig. 72); α-Fe_2O_3 is paramagnetic, while γ-Fe_2O_3 is ferromagnetic.

The *hydroxide* $Fe(OH)_3$, obtained as a reddish-brown precipitate, has a varying $Fe_2O_3 \cdot nH_2O$ composition. Dehydration results in intermediate high-molecular -ol and oxol compounds of an FeOOH composition (which are the basis of several iron minerals), and finally Fe_2O_3.

Fe_2O_3 and $Fe_2O_3 \cdot nH_2O$ are soluble in acids, forming pale violet $[Fe(OH_2)_6]^{3+}$ aquo complexes. Crystal hydrates $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \times \times 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Fe(ClO_4)_3 \cdot 10H_2O$, and $\overset{+1}{M}Fe(SO_4)_2 \cdot 12H_2O$ (iron alum) are precipitated from acid solutions. The dehydrated compounds have a different colour, depending on the anion's nature: namely FeF_3 greenish, $FeCl_3$ blackish brown, and $Fe(CNS)_3$ blood red.

In neutral solutions the salts of Fe(III) are strongly hydrolysed and the solutions become yellowish-brown in colour; the initial stages of this can be described by the following equations:

$$[Fe(OH_2)_6]^{3+} + H_2O \rightleftarrows [Fe(OH_2)_5OH]^{2+} + OH_3^+, \quad K = 10^{-3.05}$$

$$[Fe(OH_2)_5OH]^{2+} + H_2O \rightleftarrows [Fe(OH_2)_4(OH)_2]^{+} + OH_3^+, \quad K = 10^{-3.26}$$

$$2[Fe(OH_2)_6]^{3+} \rightleftarrows \left[\begin{array}{ccccc} & H_2O & H & OH_2 & \\ H_2O & | & O & | & OH_2 \\ & Fe & & Fe & \\ H_2O & | & O & | & OH_2 \\ & H_2O & H & OH_2 & \end{array}\right]^{4+} + 2OH_3^+, \quad K = 10^{-2.91}$$

Subsequent polymerisation of the hydroxyaquocomplexes (especially with heating) forms polynuclear complexes, the derivatives of which separate out from the solution in a colloidal state. Finally $Fe_2O_3 \cdot nH_2O$ precipitates as a brownish-red jelly-like mass.

The *ammoniates* of Fe(III) of the type of $[Fe(NH_3)_6]Hal_3$ are even less stable than those of Fe(II) and are completely decomposed by water.

The *anion* complexes of Fe(III) are more stable than those of Fe(II) and easier to obtain; freshly obtained $Fe(OH)_3$ ($Fe_2O_3 \cdot nH_2O$), for instance, is noticeably soluble in concentrated alkalis, forming hexahydroxyferrates(III) of the type of $\overset{+1}{M}_3[Fe(OH)_6]$. Fusing of Fe_2O_3 or $Fe(OH)_3$ with alkalis or carbonates of the alkali metals results in oxyferrates(III) of the type of $\overset{+1}{M}FeO_2$, known as *ferrites*:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2$$

Oxy- and hydroxyferrates(III) of Group I and II *s* elements (yellow or red) are decomposed by water.

The *mixed* oxide, black *magnetite* Fe_3O_4, can be regarded as an oxymetaferrate(III) of iron(II), $\overset{+2}{Fe}(FeO_2)_2$.

In magnetite crystals, the Fe(II) atoms are in an octahedral configuration of oxygen atoms and the Fe(III) atoms in octahedral and tetrahedral ones. Ferrites of the other *d* elements have a similar structure.

Magnetite and $\overset{+2}{M}(FeO_2)_2$ ferrites (in which M is Mn, Co, Ni, Cu) are ferromagnetic. They are used in electrical engineering, and in particular in the manufacture of magnetic recording tapes.

Other compounds of iron(III) also display acidic properties, corresponding to ferrates(III) of the type of $\overset{+1}{M}_3[FeF_6]$, $\overset{+1}{M}[FeCl_4]$, $\overset{+1}{M}_3[Fe(CNS)_6]$, etc. The most stable anion complex of Fe(III) is the hexacyanoferrate(III) $[Fe(CN)_6]^{3-}$ (K_{st} 8×10^{43}). Unlike most other Fe(III) complexes, which are high-spin, this ion is a low-spin complex: $(\sigma)^{12}\ (\pi_d^{non})^5$. Its derivatives are obtained by oxidising hexacyanoferrates(II). The most important cyanoferrate(III) is $K_3[Fe(CN)_6]$ (potassium ferricyanide, or *red prussiate of potash*). In particular, it is the reagent for the Fe^{2+} ion, with which it gives a deep blue barely soluble hexacyanoferrate(III) of potassium(I) and iron(II), known as *Turnbull's blue*:

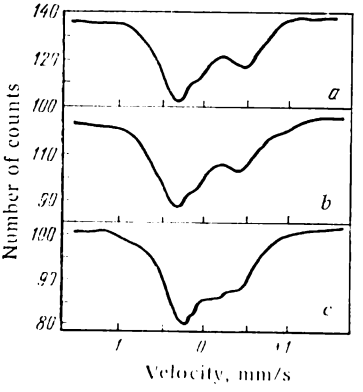


Fig. 237. γ Spectra of Berlin blue (*a*), Turnbull blue (*b*) and salts $K\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]$ and $K\overset{+2}{Fe}[\overset{+3}{Fe}(CN)_6]$ (*c*)

$$FeCl_2 + K_3[Fe(CN)_6] = KFe[Fe(CN)_6] + 2KCl$$

or

$$Fe^{2+} + K^+ + [Fe(CN)_6]^{3-} = K\overset{+2}{Fe}[\overset{+3}{Fe}(CN)_6]$$

X-ray crystallography shows that Turnbull's blue and Berlin blue have the same cubic lattice with the iron atoms in equivalent position. It has also been shown that their γ-resonance spectra are practically the same (Fig. 237), all of which indicates that they are completely identical and can be described by the formula $KFe[Fe(CN)_6]$. The Fe(II) atoms are surrounded by the carbon atoms and the Fe(III) atoms by the nitrogen atoms of the cyanide groups. Thus the salt $KFe(Fe(CN)_6]$ is formed by a polymeric coordination ion $[Fe_2(CN)_6]^-$ with a structure close to that of ReO_3. In contrast to the complex cyanides, $Fe(CN)_3$ is unknown.

Compounds of Fe(III) have oxidising properties:

$$Fe^{3+} + e^- = Fe^{2+}, \quad E^\circ_{298} = 0.77\ V$$

$$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}, \quad E^\circ_{298} = 0.36\ V$$

Being an oxidant, $[Fe(CN)_6]^{3-}$ oxidises hydrogen peroxide

$$2[Fe(CN)_6]^{3-} + H_2O_2 + 2OH^- = 2[Fe(CN)_6]^{4-} + O_2 + 2H_2O$$

Because of the oxidising action of Fe(III), FeI_3 and $Fe(CN)_3$ are unstable. Attempts to obtain them end in a redox reaction in the solutions, as for example,

$$2FeCl_3 + 6KI = 2FeI_2 + I_2 + 6KCl$$

For the same reason, it is impossible to precipitate Fe_2S_3 from Fe(III) solutions, but when H_2S or a sulphide is added to the $\overset{3+}{Fe}$ solution, a precipitate containing FeS and colloidal sulphur is formed.

Compounds of the $\overset{+1}{M}_3[E(CN)_6]$ and $\overset{+1}{M}_3[ECl_6]$ type are known for ruthenium(III) and osmium(III).

Compounds of iron(IV), ruthenium(IV), and osmium(IV). The +4 oxidation state is more typical of ruthenium and osmium. Oxides, halides, and numerous derivatives of anion complexes with the general formula $\overset{+1}{M}_2[EX_6]$, e.g. $\overset{+1}{M}_2[ECl_6]$, $\overset{+1}{M}_2[ECl_3Br_3]$, and $\overset{+1}{M}_2[EBr_6]$ are known.

The *oxides* and *hydroxides* of Ru(IV) and Os(IV) are predominantly acidic. Thus the EO_2 dioxides (black) are insoluble in water but react with hydrohalic acids

$$EO_2 + 6HCl = H_2[ECl_6] + 2H_2O$$

Anion complexes are also formed during hydrolysis of the tetrahalides:

$$3EF_4 + 2H_2O = EO_2 + 2H_2[EF_6]$$

Oxyferrates(IV) of the type of $\overset{+2}{M}FeO_3$, $\overset{+1}{M}_2FeO_3$, and $\overset{+2}{M}_2FeO_4$ are known for iron(IV). They are black or dark grey powders, stable at room temperature and in the absence of moisture. They are isotypical in structure to the corresponding oxytitanates(IV). Oxyferrates(IV) are strong oxidants, oxidising, for example, concentrated hydrochloric acid. Oxyferrates(IV) can be obtained by oxidation of oxyferrates(III) in a stream of oxygen with heating.

Compounds of iron(VI), ruthenium(VI), and osmium(VI). Iron and ruthenium have an oxidation state of +6 in their tetrahedral EO_4^{2-} anion complexes, and osmium in the octahedral ion $[OsO_2(OH)_4]^{2-}$. The tetraoxyferrates(VI), tetraoxyruthenates(VI) and tetrahydroxydioxyosmates(VI) are formed by oxidation of the metals or the corresponding compounds in a strongly alkaline medium, e.g.

$$Fe_2O_3 + 3KNO_3 + 4KOH \underset{\text{fusion}}{=\!=} 2K_2FeO_4 + 3KNO_2 + 2H_2O$$

The oxyferrates(VI) are crystalline substances, usually red, isomorphic in structure with the corresponding oxychromates(VI) and oxysulphates(VI), and form solid solutions with them. Their solubility is also close to those of the corresponding chromates and sulphates. In particular, the oxyferrates(VI) of the alkali metals and calcium are soluble like the oxychromates and oxysulphates; the oxyferrates of barium and strontium are insoluble. Most of them decompose in solution or when slightly heated, liberating oxygen. Oxyferrates(VI) are strong oxidants, superior in this respect to oxymanganates(VII). They oxidise H_3N, for example, to NO_3^-, $Cr(OH)_4^-$ to CrO_4^{2-}, and AsO_3^{3-} to AsO_4^{3-}, and so on.

The oxidising properties of orange oxyruthenates(VI) are less marked, but even they oxidise concentrated hydrochloric acid. On the contrary, in accordance with the stable oxidation state of osmium, pink hydroxydioxyosmates(VI) are quite readily oxidised to OsO_4

$$2K_2[OsO_2(OH)_4] + O_2 = 2OsO_4 + 4KOH + 2H_2O$$

Compounds of the type of H_2EO_4 (*ferric*, *ruthenic*, and *osmic* acids) and EO_3 have not been obtained; under the action of acids, oxyferrates(VI), oxyruthenates(VI) and hydroxyosmates(VI) are decomposed, e.g.

$$2Na_2RuO_4 + 2H_2SO_4 = 2Na_2SO_4 + 2RuO_2 + O_2 + 2H_2O$$

Ruthenates(VI) and osmates(VI) of the type of $\overset{+1}{M}_2[EO_2Hal_4]$ and $\overset{+1}{M}_2[OsNHal_5]$ have also been obtained.

The only binary E(VI) compounds known are the hexafluorides RuF_6 (brown, m.p. 54° C) and OsF_6 (yellow-green, m.p. 33.2 °C). They are very reactive and easily dissociate into fluorine and lower fluorides.

Compounds of ruthenium(VIII) and osmium(VIII). Tetroxides are known for ruthenium and osmium. They have molecular lattices composed of tetrahedral EO_4 molecules and are therefore low-melting (m.p. 30 °C to 40 °C), volatile substances. RuO_4 is orange-yellow while OsO_4 is colourless. The EO_4 molecules have the following electron configuration (without the 2*s* electrons of oxygen)

$$[\sigma]^8\,[\pi]^{10}\,[\pi^{non}]^6$$

Ruthenium tetroxide is obtained by oxidising ruthenates(VI):

$$Na_2RuO_4 + Cl_2 = RuO_4 + 2NaCl$$

Osmium tetroxide is quite easily obtained by oxidising osmium or its compounds by oxygen, nitric acid, or other oxidants. OsO_4 is moderately soluble in water but does not form definite compounds with it. Its acidic properties are exhibited in reaction with basic compounds: with concentrated alkalis it yields osmates(VIII) of the type of $\overset{+1}{M}_2[OsO_4(OH)_2]$ (from yellow to brown) and with fluorides of the alkali metals red-brown $\overset{+1}{M}_2[OsO_4F_2]$:

$$OsO_4 + 2KOH = K_2[OsO_4(OH)_2], \quad OsO_4 + 2KF = K_2[OsO_4F_2]$$

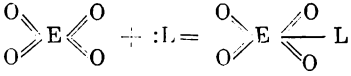
When concentrated KOH and H_3N act simultaneously on OsO_4, the osmate(VIII) of the $K[OsO_3N]$ type (yellow crystals) is formed:

$$OsO_4 + KOH + H_3N = K[OsO_3N] + 2H_2O$$

Other types of osmates(VIII) are also known. Ruthenates(VIII) are unstable compounds; RuO_4 dissolves in alkalis, liberating oxygen:

$$2RuO_4 + 4NaOH = 2Na_2RuO_4 + O_2 + 2H_2O$$

EO_4 can combine with donor-molecules L furnishing electron pairs:



The interaction of OsO_4 and liquid H_3N, for example, leads to the formation of volatile $OsO_4 \cdot NH_3$. Compounds of the type of $RuO_4 \cdot PR_3$ (in which R = F or an organic ligand) are more stable. Ruthenium

and osmium are converted into a state with a valency of nine in these reactions.

RuO_4 is a strong oxidant. It oxidises concentrated hydrochloric acid, explodes with alcohols, and also when heated, breaking down into RuO_2 and oxygen.

Iron tetroxide FeO_4 (isoelectronic with VO_4^{3-}, CrO_4^{2-}, and MnO_4^-) has not been obtained because it has a very high electron affinity and is converted into the FeO_4^{2-} ion.

The tetroxides of osmium and ruthenium are poisonous. OsO_4 has an odour resembling chlorine and RuO_4 one resembling ozone. OsO_4 is the most important osmium compound. It is used as a mild oxidant and catalyst in organic synthesis (e.g. in the synthesis of cortisone) and for staining animal tissues for microscopic examination.

7.3. The Cobalt Subgroup

Cobalt Co, rhodium Rh, and iridium Ir are full electron analogues.

	$_{27}$Co	$_{45}$Rh	$_{77}$Ir
Atomic mass	58.933	102.905	192.2
Valence electrons	$3d^74s^2$	$4d^85s^1$	$5d^76s^2$
Metallic atom radius, nm	0.125	0.134	0.135
Conventional ion E^{2+} radius, nm	0.078	—	0.089
Conventional ion E^{3+} radius, nm	0.064	0.065	0.065
Conventional ion E^{4+} radius, nm	—	0.071	0.075
Ionisation energy $E^0 \rightarrow E^+$, eV	7.87	7.46	9.1
Abundance, mole per cent	1.5×10^{-3}	1.7×10^{-7}	8.5×10^{-9}
Natural stable isotopes	^{59}Co (100%)	^{103}Rh (100%)	^{191}Ir (38.5%) ^{193}Ir (61.5%)

The pairing of $(n-1)\,d$ electrons and stabilisation of the $(n-1)\,d$ subshell go further in cobalt and its analogues than in elements of the iron subgroup. The highest oxidation state of cobalt and its analogues is therefore lower than that of iron, ruthenium, and osmium. The most typical oxidation states of cobalt are +2 and +3; for iridium the oxidation states +3 and +4 are roughly equivalent. Compounds of rhodium(VI) and iridium(VI) have also been obtained. The coordination numbers of six and four are stable with the elements of this subgroup (see Table 52).

Cobalt and rhodium occur in one stable isotope and iridium in two, but many artificial radioactive isotopes have been obtained, e.g. ^{60}Co (half-life 5.24 years) by the reaction

$$^{59}\mathrm{Co}\ (n,\ \gamma)^{60}\mathrm{Co}$$

^{60}Co is used in medicine (in the cobalt gun) to treat cancer.

Pure cobalt ores are rarely found; *cobaltite* (*cobalt glance*) CoAsS is relatively more common. Cobalt occurs in certain copper, nickel,

Table 52. **Oxidation States and Spatial Configurations of Complexes (Unit Cells) of the Cobalt Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical compounds
−1		4	Tetrahedron	$[Co(CO)_4]^-$, $[Rh(CO)_4]^-$
0	d^9	6	Tetrahedron	$Co_2(CO)_8$
+2	d^7	4	Tetrahedron	$[CoCl_4]^{2-}$, Co (II) in Co_3O_4
		6	Octahedron	$CoCl_2$, $[Co(NH_3)_6]^{2+}$, $[Co(OH_2)_6]^{2+}$
+3	d^6	6	Octahedron	$[E(NH_3)_6]^{3+}$, $[E(CN)_6]^{3-}$, $[CoF_6]^{3-}$ $[RhCl_6]^{3-}$, $[IrCl_6]^{3-}$, RhF_3, IrF_3
+4	d^5	6	Octahedron	$[EF_6]^{2-}$, $[IrCl_6]^{2-}$, IrO_2
+6	d^3	6	Octahedron	RhF_6, IrF_6

silver, iron, manganese, and polymetallic ores. It is also contained in animal and plant tissues.

Iridium usually occurs as an alloy with osmium (osmiridium) and also (like rhodium) in native platinum and in copper-nickel polymetallic ores.

The simple substances. As the simple substances, cobalt, rhodium, and iridium are white lustrous metals, cobalt having a greyish tinge, and rhodium and iridium a silvery one. Cobalt is harder and more brittle than iron. Rhodium and iridium are very hard. The main constants of these metals are as follows:

	Co	Rh	Ir
Density, g/cm³	8.84	12.44	22.4
M.p., °C	1492	1963	2450
B.p., °C	~ 2880	~ 3700	~ 4100
Electrical conductivity	108	19	16
E°_{298}, $E^{2+}+2e^-=E$, V	−0.27	0.6	1.1
$\Delta H^\circ_{\text{subl., 298}}$, kJ/mol	425	447	669
S°_{298}, J/K·mol	30.04	31.5	35.5

Cobalt has two allotropic forms. Alpha cobalt (hexagonal lattice) is stable at temperatures under 417 °C and beta cobalt (face-centred cubic lattice) above 417 °C. Rhodium and iridium have face-centred cubic lattices.

Cobalt is slightly less active chemically than iron. In normal conditions it is quite stable and only begins to be oxidised by oxygen, for example, at 300 °C. When heated, it reacts with almost all nonmetals, forming compounds, like iron, from salt-like ($CoHal_2$) to the metallic (Co_3C, Co_2B, and Co_2N), and solid solutions (with H, B,

and O). Cobalt is also slightly more stable toward acids. It practically does not react with alkalis.

Rhodium and especially iridium are chemically very stable. They react with nonmetals in a finely divided state when red-hot. Rhodium begins to oxidise in air only at 600 °C and iridium at temperatures above 1000 °C:

$$2\overset{0}{\mathrm{Rh}}\,(c) + 3/2O_2\,(g) = \overset{+3}{\mathrm{Rh}_2}O_3\,(c), \quad \Delta G^\circ_{298} = -277\ \mathrm{kJ}$$

$$\overset{0}{\mathrm{Ir}}\,(c) + O_2\,(g) = \overset{+4}{\mathrm{IrO}_2}\,(c), \quad \Delta G^\circ_{298} = -188\ \mathrm{kJ}$$

Unlike the other noble metals, compact Rh and Ir are practically insoluble in acids or mixtures of acids. They can be converted into water-soluble compounds by chlorination of a mixture of the finely divided red-hot metal and NaCl:

$$\overset{0}{\mathrm{Ir}} + 2Cl_2 + 2NaCl = Na_2\overset{+4}{[\mathrm{IrCl}_6]}$$

Cobalt, rhodium, and iridium form solid solutions and intermetallic compounds with the corresponding metals, which determines the physicochemical and mechanical properties of their various alloys. Alloys of cobalt are very widely used. Many of them are high-melting and heat-resistant; one—*vitallum* (65% Co, 28% Cr, 3% Ni and 4% Mo)—for example, used in jet engines and gas turbines, retains its high strength and is practically unaffected by gases at temperatures of 800 °C to 900 °C. There are also acid-resistant cobalt alloys that rival platinum. Cobalt alloys like *Alnico* (50% Fe, 24% Co, 14% Ni, 9% Al and 3% Cu) are used in permanent magnets. The *extra-hard alloys*, which are cobalt-cemented carbides of tungsten (WC alloys) and titanium (TiC alloys), are of great value for making cutting tools. Cobalt is of major importance as alloying additive for steels.

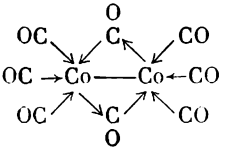
As a rule, cobalt is obtained by refining polymetallic ores. Co_3O_4 is isolated by a series of pyrometallurgical processes and the cobalt is then reduced by carbon or hydrogen, occasionally by aluminium. Cobalt of special purity is obtained by electrorefining, and by thermal decomposition of certain cobalt compounds.

Most of the cobalt produced is used for alloying metals. It is also used for electroplating metal parts.

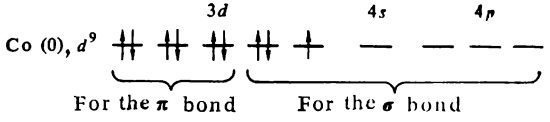
The high corrosion resistance and hardness of rhodium and iridium account for their use in the manufacture of most important parts of measuring instruments. Rhodium, which has high light-reflecting properties is used in the manufacture of mirrors and reflectors. Platinum rhodium alloys are used as catalysts of the oxidation of ammonia in the manufacture of nitric acid.

7.4. Compounds of the Cobalt Subgroup Elements

Compounds of cobalt(0), rhodium(0), and iridium(0). Carbonyls of cobalt(0) and its analogues are known. The simplest is $Co_2(CO)_8$, a dinuclear compound:



The structure of its molecule can be explained as follows. The cobalt atoms form six σ bonds, four of them through a donor-acceptor interaction of electron pairs of four of the CO molecules and the free orbitals of Co. The fifth is formed by a *d* electron pair of the Co atom and a free π orbital of a CO molecule. The Co—Co bond is formed by unpaired electrons of the two cobalt atoms. The molecule is stabilised by π bonds that are formed from the $3d_\varepsilon^6$ electrons of the cobalt atom



The octacarbonyl $Co_2(CO)_8$ is obtained by heating powdered Co in an atmosphere of CO (at 150 °C to 200 °C and 2.5 × 10^7 Pa). The octacarbonyl is an orange crystalline solid (m.p. 51 °C), insoluble in water but readily soluble in organic solvents. At 60 °C the cobalt octacarbonyl begins to decompose.

When heated under pressure in an atmosphere of hydrogen, $Co_2(CO)_8$ forms hydrocarbonyl (carbonyl hydride), which can be regarded as a derivative of cobalt in the —1 oxidation state:

$$Co_2(CO)_8 + H_2 = 2H[Co(CO)_4]$$

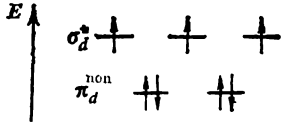
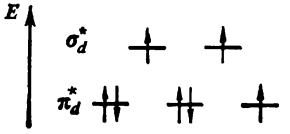
Salts of the type of $K[Co(CO)_4]$ and $NH_4[Co(CO)_4]$ are also known. Unlike them, the derivatives of the type of $Zn[Co(CO)_4]_2$ and $Ga[Co(CO)_4]_3$ are covalent compounds—mixed carbonyls of a cluster type with M—Co bonds.

The strength of the acids increases in the hydrocarbonyl series $HMn(CO)_5$—$H_2Fe(CO)_4$—$HCo(CO)_4$, but they become less stable. $[Rh(CO)_4]^-$ derivatives are also known.

The tetranuclear carbonyl $Co_4(CO)_{12}$ (black, decomposing at 60 °C) and liquid $Co(NO)(CO)_3$ and $Co(NO)(PF_3)_3$ have been obtained

for cobalt(0). Carbonyls of rhodium and iridium with a composition of $E_2(CO)_8$, $E_4(CO)_{12}$, and $E_6(CO)_{16}$ have been obtained.

Compounds of cobalt(II). A +2 oxidation state is characteristic of cobalt. Its stable coordination numbers are six and four, which correspond to an octahedral and tetrahedral distribution of the σ bonds. Most compounds of cobalt(II) are paramagnetic:

Distribution of electrons in σ_d^* and π_d^{non} MO	Typical compounds
	High-spin octahedral complexes $Co(OH_2)_6^{2+}$, $Co(NH_3)_6^{2+}$, CoF_6^{4-}
	Tetrahedral complexes $CoCl_4^{2-}$, $CoBr_4^{2-}$, $Co(CNS)_4^{2-}$

Unlike Fe(II) and most other *d* elements of the fourth period, the tetrahedral complexes of Co(II) are most varied.

An octahedral unit cell is the basis of the coordination crystals of CoO (NaCl type) and CoF_2 (rutile type), and of the layered crystals of $CoCl_2$ and $Co(OH)_2$ (see Fig. 232).

Cobalt(II) oxide CoO is a greyish-green crystalline solid formed by interaction of the simple substances or by thermal decomposition of $Co(OH)_2$ and $CoCO_3$. Dihalides $CoHal_2$ are also formed by the simple substances, or by dehydration of the corresponding crystal hydrates. The dihalides (except CoF_2) are soluble in water. The hydroxide $Co(OH)_2$ exists in blue and pink forms. The blue form is obtained by the action of alkalis on Co(II) salts in the cold; when heated $Co(OH)_2$ is converted into its pink form. $Co(OH)_2$ is insoluble in water. It is amphoteric by chemical nature (like CoO), with predominantly basic properties.

Aquo complexes $[Co(OH_2)_6]^{2+}$, which colour the solution bright pink, are the most characteristic *cation* complexes of Co(II). Its crystal hydrates $Co(NO_3)_2 \cdot 6H_2O$, $CoSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, etc., which are also pink (or red), are formed by the interaction of CoO or $Co(OH)_2$ and acids.

When heated, or acted upon by dehydrating agents ($CaCl_2$, alcohol, etc.), the colour of Co(II) crystal hydrates changes, which is connected with a change in the character of the coordination of the ligands and the generation of poly-

nuclear complexes. The heating of crystal hydrates of $CoCl_2$, for example, is accompanied with the following changes in their composition and colour:

$$\underset{\text{Pink}}{CoCl_2 \cdot 6H_2O} \xrightarrow{49\ ^\circ C} \underset{\text{Pink}}{CoCl_2 \cdot 4H_2O} \xrightarrow{58\ ^\circ C} \underset{\text{Blue-violet}}{CoCl_2 \cdot 2H_2O} \xrightarrow{90\ ^\circ C} \rightarrow$$

$$\rightarrow \underset{\text{Blue}}{CoCl_2 \cdot H_2O} \xrightarrow{140\ ^\circ C} \underset{\text{Blue}}{CoCl_2}$$

The process is reversed by the action of water on anhydrous chloride $CoCl_2$, crystal hydrates of Co(II) being formed. An aqueous solution of $CoCl_2$ is used in the manufacture of the test paper that is used for the determination of moisture (the dry paper is blue; when moistened it becomes pink).

The colour change is due to the altered coordination of the water molecules and the chloride ions around the atom of Co(II), and hence due to the change in the value of Δ. The unit cells of the pink crystals of $CoCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 4H_2O$ are $[Co(OH_2)_4Cl_2]$ octahedra, the blue-violet crystals of $CoCl_2 \cdot 2H_2O$ are $[Co(OH_2)_2Cl_4]$ octahedra; those of the blue crystals of $CoCl_2 \cdot H_2O$ and $CoCl_2$ are $CoCl_6$ octahedra.

Anhydrous halides, thiocyanate, sulphate, and other derivatives can combine with ammonia molecules to form a hexa-ammino complex $[Co(NH_3)_6]^{2+}$. The ammoniates of Co(II) are more stable than those of Fe(II) but are still decomposed by water:

$$[Co(NH_3)_6]Cl_2 + 2H_2O \rightleftharpoons Co(OH)_2 + 4H_3N + 2NH_4Cl$$

They are therefore formed in solution in the presence of NH_4Cl and a large excess of ammonia.

Ammoniates of Co(II) are easily oxidised in solution even by the molecular oxygen of air through transition to the low-spin complex of Co(III):

$$[Co(NH_3)_6]^{3+} + e^- = [Co(NH_3)_6]^{2+}, \quad E^\circ_{298} = 0.1\ V$$

$$4[Co(NH_3)_6]^{2+} + O_2 + 2H_2O = 4[Co(NH_3)_6]^{3+} + 4OH^-$$

The *anion* complexes of Co(II) usually have a $[CoX_4]^{2-}$ tetrahedral structure (where X = Cl^-, Br^-, I^-, CNS^-, OH^-). These are blue or violet substances formed by the interaction of the corresponding compounds of Co(II) and similar basic compounds. When $Co(OH)_2$ is heated in concentrated alkalis, $[Co(OH)_4]^{2-}$ is formed

$$2NaOH + Co(OH)_2 = Na_2[Co(OH)_4]$$

while $[CoCl_4]^{2-}$ is formed by the interaction of concentrated solutions of $CoCl_2$ and hydrochloric acid. In the presence of basic halides, $\overset{+1}{M}_2[CoCl_4]$ salts can be isolated from hydrochloric solutions of $CoCl_2$.

Most derivatives of the anion complexes of Co(II)—the cobaltates $\overset{+1}{M}_2[CoHal_4]$, $\overset{+1}{M}_2[Co(OH)_4]$, $\overset{+1}{M}_2[Co(CNS)_4]$, etc., are double salts (as regards stability). When solutions of them are diluted, the $[CoX_4]^{2-}$ ions are usually decomposed. The blue thiocyanate cobaltate(II) is formed by the following reaction

$$2KCNS + Co(CNS)_2 = K_2[Co(CNS)_4]$$

which is employed in analytical chemistry to identify cobalt(II). When $K_2[Co(CNS)_4]$ is strongly diluted with water, the compound is decomposed (log $K_{st} = -0.3$) and its colour changes to pink through the formation of $[Co(OH_2)_6]^{2+}$ ions:

$$[Co(CNS)_4]^{2-} + 6H_2O \rightleftarrows [Co(OH_2)_6]^{2+} + 4CNS^-$$

These octahedral ions are high-spin complexes with the following electron configuration

$$[\sigma]^{12}[\pi_d^{non}]^5[\sigma_d^*]^2$$

Low-spin octahedral complexes with the following electron configuration

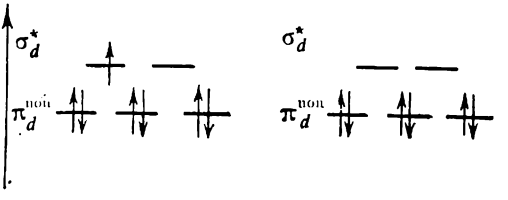
$$[\sigma]^{12}[\pi_d^{non}]^6[\sigma_d^*]^1$$

are not typical of Co(II). They are strong reductants, for example,

$$[Co(CN)_6]^{3-} + 1e^- = [Co(CN)_6]^{4-}, \quad E^0 = -0.83 \text{ V}$$

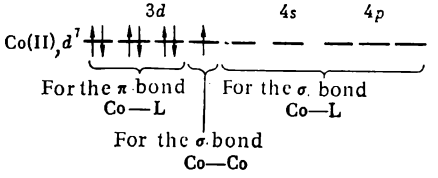
This can be explained by the high energy level of the σ^* orbital (owing to the high value of Δ). The electron is therefore easily removed from the σ^* orbital and low-spin octahedral complexes of Co(III) are formed:

$$[Co(CN)_6]^{4-} - 1e^- \rightarrow [Co(CN)_6]^{3-}$$



Dimeric complexes with the metal—metal bonds are more typical of Co(II) (as of other atoms and ions with a d^7 configuration and CN^- type strong-field

ligands):



The complex cyanides of Co(II) therefore differ from those of Fe(II). When KCN is added to solutions of Co(II), a purple salt with a composition of $K_6[Co_2(CN)_{10}]$ can be obtained. The $[Co_2(CN)_{10}]^{6-}$ complex has a structure similar to that of $Mn_2(CO)_{10}$.

High-spin complexes, on the contrary, have low values of Δ, and the energy difference between σ* and π_d^{non} orbitals is insignificant. The high-spin complex CoF_6^{4-} is oxidised only by powerful oxidants:

$$2K_4CoF_6 + F_2 = 2KF + 2K_3CoF_6$$

$$[CoF_6]^{4-} - 1e^- \rightarrow [CoF_6]^{3-}$$

Compounds of cobalt(III), rhodium(III) and iridium(III). Numerous cation, anion, and neutral complexes are very characteristic of cobalt, rhodium and iridium in the +3 oxidation state, in which the coordination number of the metals is six. Almost all are diamagnetic; the CoF_6^{3-} is paramagnetic (see Table 53).

Table 53. **Characteristics of E(III) Octahedral Complexes**

Complex	Electron configuration	Δ, kJ/mol	Magnetic properties
$[CoF_6]^{3-}$	$[\sigma]^{12}[\pi_d^{non}]^4[\sigma_d^*]^2$	155	Paramagnetic
$[Co(NH_3)_6]^{3+}$	$[\sigma]^{12}[\pi_d^{non}]^6$	273	Diamagnetic
$[Co(CN)_6]^{3-}$	Ditto	406	Diamagnetic
$[RhCl_6]^{3-}$	Ditto	241	Diamagnetic
$[Rh(NH_3)_6]^{3+}$	Ditto	407	Diamagnetic
$[IrCl_6]^{3-}$	Ditto	297	Diamagnetic
$[Ir(NH_3)_6]^{3+}$	Ditto	477	Diamagnetic

Binary compounds and salts are not characteristic of Co(III). Brown Co_3O_4, which is a mixed oxide $\overset{+2}{Co}\overset{+3}{Co}_2O_4$, is only relatively stable. It is obtained by careful heating of $Co(NO_3)_2$. The oxide is a strong oxidant.

Oxides E_2O_3, hydroxides $E(OH)_3$ (or rather $E_2O_3 \cdot nH_2O$), halides $EHal_3$, and certain other compounds (e.g. salts of the $E_2(SO_4)_3$ and $Rh(NO_3)_3$ type) are known for rhodium(III) and iridium(III)

Compounds of Ir(III) are more or less readily oxidised to Ir(IV) compounds; $Ir(OH)_3$, for example, is converted to $Ir(OH)_4$ on exposure to air; when heated to 400 °C Ir_2O_3 undergoes disproportionation and breaks up into IrO_2 and Ir. All compounds of these elements are coloured. The aquo complexes of Co(III) are unstable because they are strong oxidants:

$$[Co(OH_2)_6]^{3+} + 1e^- = [Co(OH_2)_6]^{2+}, \quad E^0_{298} = 1.81 \text{ V}$$

$[Co(OH_2)_6]^{3+}$ ion even oxidises water, so that oxygen is liberated when Co_3O_4 reacts with acids:

$$2\overset{+3}{Co}Co_2O_4 + 12H^+ + 30H_2O = 6[Co(OH_2)_6]^{2+} + O_2$$

When it reacts with concentrated hydrochloric acid, chlorine is evolved.

The numerous ammine cation complexes of Co(III) and its analogues are quite stable. The yellow hexa-amine ion $[Co(NH_3)_6]^{3+}$, for example, is not dissociated in solution to an appreciable degree ($K_{st} = 2 \times 10^{35}$), is stable in concentrated HCl, and is only slowly decomposed by H_2S and NaOH. The $[Co(NH_3)_6]^{3+}$ ion forms many readily crystallising salts with a whole number of anions for which simple derivatives of Co(III) are not known.

Many cation complexes are known for cobalt(III) and its analogues in which the NH_3 groups are partly replaced by other ligands, e.g. $[E(NH_3)_5(OH_2)]X_3$, $[E(NH_3)_5X]X_2$, $[E(NH_3)_4X_2]X$, etc. (where X is usually Cl^-, or NO_2^-). The colour of the complexes varies accordingly: e.g. $[Co(NH_3)_5(OH_2)]^{3+}$ is red, $[Co(NH_3)_5Cl]^{2+}$ is crimson, while $[Co(NH_3)_4Cl_2]^+$ may be either green (*trans*-isomer) or blue (*cis*-isomer).

There are very many compounds of the type of $\overset{+1}{M}_3[E(CN)_6]$ and $\overset{+1}{M}_3[E(NO_2)_6]$ among the cobaltates(III), rhodiates(III), and iridates(III); they are often very stable.

Examples of hexanitrite cobaltates(III) are derivatives of elements of the potassium subgroup $\overset{+1}{M}_3[Co(NO_2)_6]$, which are difficult to dissolve in water. The formation of a yellow precipitate $K_3[Co(NO_2)_6]$ is often used in analysis to detect the K^+ ion. The hexanitrite rhodiates(III) and hexanitrite iridates(III) of potassium and its analogues and NH_4^+ are also not very soluble.

The interaction of derivatives of Co(II) and KCN in the presence of an oxidant yields a pale yellow potassium hexacyanocobaltate(III) $K_3[Co(CN)_6]$. A strong, tribasic acid $H_3[Co(CN)_6]$ has also been obtained. Pale yellow $K_3[Rh(CN)_6]$ and colourless $K_3[Ir(CN)_6]$ resemble hexacyanocobaltate(III) in many properties.

Unlike the halide complexes of Co(III), the complex halides of Rh(III) and Ir(III) are very stable. Thus, the interaction of $RhCl_3$ and HCl yields a readily soluble *hexachlororhodic acid* $H_3[RhCl_6]$,

the salts of which (hexachlororhodites) are usually bright red. Green sodium hexachloroiridate(III) $Na_3[IrCl_6]$ is the initial material for other iridium(III) derivatives. It is obtained by reducing $Na_2[IrCl_6]$. Only $K_3[CoF_6]$ has been obtained for Co(III). Double sulphates of the type of $M^{+1}E(SO_4)_2 \cdot 12H_2O$ (alums) are also known.

Apart from cation and anion complexes, many neutral complexes are known for Co(III) and its analogues, which can be regarded as intermediate products in the transition from cation to anion complexes, e.g. in the transition from $[Co(NH_3)_6]^{3+}$ to $[Co(NO_2)_6]^{3-}$:

$[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5(NO_2)]Cl_2$, $[Co(NH_3)_4(NO_2)_2]Cl$,
$[Co(NH_3)_3(NO_2)_3]$, $K[Co(NH_3)_2(NO_2)_4]$, $K_2[Co(NH_3)(NO_2)_5]$,
$K_3[Co(NO_2)_6]$

or in the transition from $[Rh(NH_3)_6]^{3+}$ to $[RhCl_6]^{3-}$:

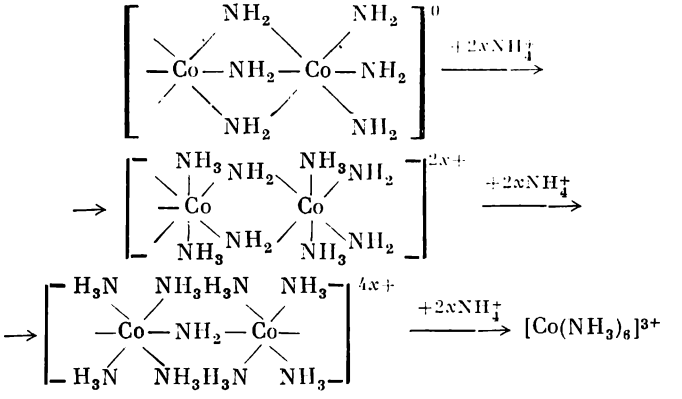
$[Rh(NH_3)_6]Cl_3$, $[Rh(NH_3)_5Cl]Cl_2$, $[Rh(NH_3)_4Cl_2]Cl$,
$[Rh(NH_3)_3Cl_3]$, $K[Rh(NH_3)_2Cl_4]$, $K_2[Rh(NH_3)Cl_5]$, $K_3[RhCl_6]$

The formation of insoluble $[Rh(NH_3)_3Cl_3]$ is used to separate Rh from the other platinum metals. Metallic rhodium can be obtained by calcining $[Rh(NH_3)_3Cl_3]$ in a current of hydrogen.

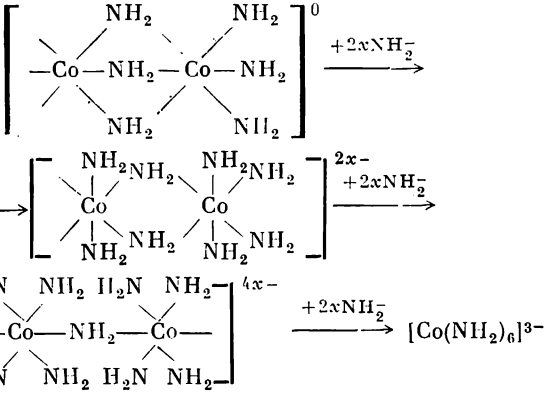
The transition from Co(III) cation complexes to anion complexes, and vice versa, can also occur in liquid ammonia. The dihydronitride (amide) $Co(NH_2)_3$, for instance, being amphoteric, reacts with both ammono acids (e.g. NH_4Cl) and ammono bases (e.g. KNH_2), which can be expressed by the following scheme:

$$[Co(NH_3)_6]^{3+} \underset{NH_4^+}{\overset{NH_2^-}{\rightleftharpoons}} Co(NH_2)_3 \underset{NH_4^+}{\overset{NH_2^-}{\rightleftharpoons}} [Co(NH_2)_6]^{3-}$$

The dissolution of polymeric $Co(NH_2)_3$ is due to gradual rupture of the amide bridges ($-NH_2-$). Coordination saturation of Co(III) is attained in ammono acids through the H_3N molecules:

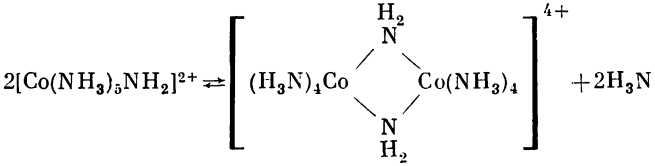


and during dissolution in ammono bases, through the NH_2 groups

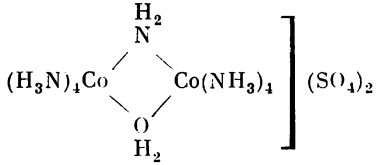


Polynuclear complexes are also formed during the ammonolysis of ammoniates of Co(III), for example,

$$[Co(NH_3)_6]^{3+} + H_3N \rightleftarrows [Co(NH_3)_5NH_2]^{2+} + NH_4^+$$



In addition, mixed hydroxydihydronitride ammine complexes are also possible:



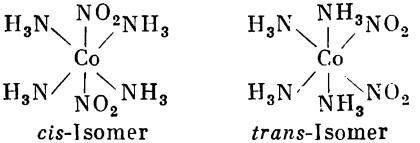
The variety of complex compounds of Co(III), Rh(III), and Ir(III) is also explained by the existence of isomeric compound; some examples are the following:

Coordination isomerism: $[Co(NH_3)_6]\ [Cr(CN)_6]$ and $[Cr(NH_3)_6] \times [Co(CN)_6]$

Hydrate isomerism: $[Co(NH_3)_4Cl_2]Cl \cdot H_2O$ and $[Co(NH_3)_4Cl(OH_2)]Cl_2$

Ionisation isomerism: $[Co(NH_3)_5SO_4]Br$ (Red) and $[Co(NH_3)_5Br]SO_4$ (Red-violet)

Geometrical isomerism:



cis-Isomer (yellow) *trans*-Isomer (brown)

Compounds of cobalt(IV), rhodium(IV), and iridium(IV). An oxidation state of +4 is characteristic of iridium. A black oxide IrO_2 and black hydroxide $Ir(OH)_4$ (or rather $IrO_2 \cdot nH_2O$), insoluble in water, and also black halides $IrHal_4$ are known for Ir(IV). The halides are completely hydrolysed in water.

The most typical complex compounds of Ir(IV) are the dark-red chlorides $\overset{+1}{M}_2[IrCl_6]$. As already remarked, they are obtained by chlorinating a mixture of powdered iridium and a basic chloride or by the interaction of IrO_2 and $\overset{+1}{M}Cl$ in hydrochloric acid:

$$IrO_2 + 4HCl + 2NaCl = Na_2[IrCl_6] + 2H_2O$$

$Na_2[IrCl_6]$ is a hexachloroiridate(IV) readily soluble in water; derivatives of the potassium subgroup elements and of NH_4^+ are poorly soluble. The formation of barely soluble $(NH_4)_2[IrCl_6]$ is used to separate iridium from the other platinum metals. When $(NH_4)_2[IrCl_6]$ is calcined in an atmosphere of hydrogen, pure iridium is obtained.

The compounds of Rh(IV) include the difficult to dissolve green caesium hexachlororhodiate(IV) $Cs_2[RhCl_6]$, which is an oxidant; chlorine is partly split off as soon as it is in contact with water.

Compounds of rhodium(VI) and iridium(VI). Iridium and rhodium display a +6 oxidation state in their hexafluorides EF_6, which are low-melting solids: RhF_6 (m.p. 70 °C) is a reddish-brown and IrF_6 (m.p. 44 °C, b.p. 53 °C) is yellow. They are prepared by oxidising the metals in an atmosphere of fluorine.

The hexafluorides, especially RhF_6, are unstable and strong oxidants that oxidise water vigorously

$$2IrF_6 + 10H_2O = 2Ir(OH)_4 + 12HF + O_2$$

In the absence of water, they even oxidise free chlorine and NO:

$$2RhF_6 + 3Cl_2 = 2RhF_3 + 6ClF$$

$$NO + IrF_6 = NO^+[IrF_6]^-$$

The most widely used derivatives of elements of the cobalt subgroup are compounds of cobalt itself. Apart from the fields already mentioned, they are used in making coloured enamels and paints. In agriculture, cobalt compounds are used as microfertilisers and to fortify animal feeds.

7.5. The Nickel Subgroup

Nickel Ni, palladium Pd, and platinum Pt have the following constants:

	$_{28}$Ni	$_{46}$Pd	$_{78}$Pt
Atomic mass	58.71	106.4	195.09
Valence electrons	$3d^84s^2$	$4d^{10}5s^0$	$5d^96s^1$
Metallic atom radius, nm	0.124	0.137	0.138
Conventional ion E^{2+} radius, nm	0.074	0.088	0.090
Conventional ion E^{4+} radius, nm	—	0.064	0.064
Ionisation energy $E^0 \rightarrow E^+$, eV	7.64	8.34	8.9
Abundance, mole per cent	3.2×10^{-3}	2×10^{-7}	5×10^{-8}

The most characteristic oxidation state of nickel and palladium is +2, and of platinum +4. Compounds of platinum(VI) are also known. The most stable coordination numbers of nickel and its analogues are four (tetrahedron or square) and six (octahedron). The oxidation states of the elements and corresponding spatial configurations of complexes are given in Table 54.

Table 54. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of the Nickel Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical compounds
0	d^{10}	4	Tetrahedron	$Ni(CO)_4$, $Ni(PF_3)_4$, $[Ni(CN)_4]^{4-}$
+2	d^8	4	Tetrahedron	$NiCl_4^{2-}$
		4	Square	$[Pt(NH_3)_4]^{2+}$, $[E(CN)_4]^{2-}$, $[PtCl_4]^{2-}$, $[Pt(NH_3)_2Cl_2]^0$, PdO, PtO, $PdCl_2$
		6	Octahedron	$[Ni(OH_2)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ $[Ni(CNS)_6]^{4-}$, NiO, NiF_2, PdF_2, NiCl
+4	d^6	6	Octahedron	$[Pt(NH_3)_6]^{4+}$, $[PtCl_6]^{2-}$, $[NiF_6]^{2-}$ $[Pt(NH_3)_2Cl_4]^0$
+6	d^1	6	Octahedron	PtF_6

Nickel is quite abundant in the Earth's crust; palladium and platinum, like the other platinum metals, are rare elements. Platinum is the most abundant metal of its family.

Nickel is usually contained in copper-nickel sulphide ores, a valuable polymetallic raw material. In addition to nickel, they also contain Cu, Ag, Au, platinum metals, and rare and dispersed elements. Platinum also occurs in native alloys containing small amounts of

other metals (Ir, Pd, Rh, Fe, sometimes Ni, Cu, etc.). Palladium occurs together with platinum. The main sources of platinum metals are platinum-containing copper-nickel sulphide ores.

The simple substances. The elements of the nickel subgroup are shiny white metals. Ni and Pt have a silvery sheen and Pd a greyish one.

Nickel forms two allotropies, hexagonal α-Ni, which exists at temperatures below 250 °C and β-Ni, which has a face-centred cubic lattice. Palladium and platinum crystallise in face-centred cubic lattices.

The most important constants of Ni, Pd, and Pt are as follows:

	Ni	Pd	Pt
Density, g/cm³	8.91	12.02	21.45
M.p., °C	1455	1552	1769
B.p., °C	~ 2840	~ 3100	~ 4000
Electrical conductivity	14	10	10
$\Delta H^\circ_{\text{subl., 298}}$, kJ/mol	424	381	556
S°_{298}, J/K·mol	29.9	37.7	41.5
E°_{298}, $E^{2+} + 2e^- = E$, V	−0.25	+0.997	+1.19

Nickel is less chemically active than either iron or cobalt. It begins to combine with oxygen at 500 °C. When heated (particularly in the powdered state) it is readily oxidised by the halogens, sulphur, selenium, phosphorus, arsenic, antimony, etc.; like other *d* elements, it forms compounds of a nonstoichiometric and variable composition with most of them. Many of these compounds are metal-like.

Compared with the other platinum metals, palladium and platinum are slightly more reactive, but they also react only when heated (often to red-hot temperatures) and in the powdered state. The compounds so obtained are unstable and decompose when heated further.

A specific feature of palladium is its power to absorb considerable amounts of hydrogen; one volume of Pd, for instance, can absorb about 900 volumes of H_2 at 80 °C. Palladium and nickel are good catalysts of hydration and reduction by hydrogen. In the presence of Pd, hydrogen converts SO_2 into H_2S, and ClO_3^- into Cl_2, and so on. Absorption of oxygen is most characteristic of platinum. The metal is of major importance as a catalyst of the oxidation of H_3N by oxygen (in the production of HNO_3), of hydrogen (to purify O_2 from H_2 admixtures), and in other catalytic oxidation processes.

Nickel comes before hydrogen in the electromotive series, and palladium and platinum after it. Nickel behaves like iron and cobalt in relation to acids and alkalis. Unlike the other platinum metals, palladium (like silver) is quite readily dissolved in concentrated nitric acid and hot concentrated sulphuric acid, while platinum (like gold) dissolves only in aqua regia with heating:

$$3\overset{0}{Pt} + 4HNO_3 + 18HCl = 3H_2[\overset{+4}{Pt}Cl_6] + 4NO + 8H_2O$$

When fused with alkalis, cyanides, and sulphides of the alkali metals in the presence of oxidants (even O_2), palladium and platinum are converted into derivatives of anion complexes.

Nickel is obtained mainly from copper-nickel sulphide ores by a complicated multistage process. A series of pyrometallurgical operations yields NiO. The free metal is obtained by reducing NiO, usually by carbon, and is then electrorefined in a solution of sulphate. The accompanying platinum metals, silver, and gold are separated from the anode sludge by a complicated process.

Around 80 per cent of the nickel produced is used for making nickel alloys and alloy steels (stainless, refractory, armour, etc.). Nickel is used to make special chemical apparatus, and also as a decorative and protective coating for other metals. Palladium and platinum are used in the manufacture of corrosion-resistant laboratory vessels, apparatus and instruments for the chemical industry, resistance thermometers, and thermocouples, and as electrical contacts. Platinum is used, for example, for insoluble anodes for the electrolytic production of persulphuric acid and perborates. Palladium and platinum are both employed in jewellery.

7.6. Compounds of the Nickel Subgroup Elements

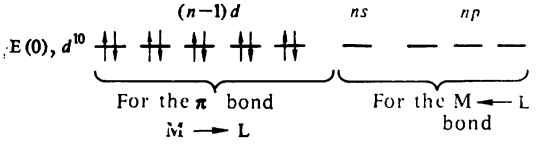
Metallic and metal-like compounds. Nickel forms continuous solid solutions with Group VIII metals (except Ru and Os), manganese, and copper. The intermetallic compounds of nickel are also quite varied, e.g. those in the Ni_3Fe—Ni_3Mn—Ni_3Cr—Ni_3V——Ni_3Ti—Ni_3Al series, such compounds are high-melting and heat-resistant and are used in rocket engineering, gas turbines, and the atomic industry. Intermetallic compounds form part of nickel alloys, imparting valuable physicochemical and mechanical properties to them.

Heat-resistant alloys of nickel are the *Inconels* (73% Ni, 15% Cr, 7% Fe, 2.4% Ti, the remainder Al, Nb, Mn, and Si), and *nimonic* (59% Ni, 20% Cr, 16% Co, 2.3% Ti, 1.4% Al, the remainder Fe, Mn, and Si). The *Nichrome*, chromium-nickel alloys, are high-melting, heat-resistant, and have high electrical resistance; some of them (e.g. that alloy containing 80% Ni and 20% Cr) are stable under the action of gases at temperatures of 1000 °C to 1100 °C. Nichromes are widely used as heating elements in electrical engineering. *Monel metal* (a solid solution of Ni with 30 per cent Cu) possesses high chemical stability and is employed for making chemical apparatus and kitchen equipment. Magnetic nickel alloys of the type of *Alnico* (see p.594), and *Alni* (22-24% Ni, 11-14% Al, the remainder Fe) etc., are widely used.

Stainless steel is an iron-nickel alloy containing 18% Cr and 8% Ni. Another iron-nickel alloy *Invar* (36% Ni, 0.5% Mn and 0.5% C) hardly expands at all when heated; *platinite* (0.15% C and 46% Ni) which has the thermal expansion coefficient of glass is used as a platinum-substitute for soldering with glass, etc.

Compounds of nickel(0), palladium(0) and platinum(0). Like other *d* elements, a zero (and also a negative) oxidation state of

nickel and its analogues (as with other *d* elements) is displayed in compounds with ligands of σ donor and π acceptor type, i.e. CO, PF_3, CN^-. The electron configuration of the central atom being d^{10}, the structure of complexes with strong-field ligands is more often a tetrahedron (Fig. 238). According to the valence bond theory, this corresponds to sp^3 hybridisation of the valence orbitals of the central atom:



A *tetracarbonyl* $Ni(CO)_4$ is known for Ni(0). In normal conditions it is a colourless liquid (f.p. −19.3 °C. b.p. 43 °C) obtained by the action of CO on nickel powder at 60 °C to 80 °C. At 180 °C it decomposes, which is utilised to obtain the pure metal and for plating metals. $Ni(CO)_4$ is also employed as a catalyst in organic synthesis. The ease with which $Ni(CO)_4$ is formed is employed to separate nickel and cobalt, since a higher temperature and pressure are required to obtain cobalt carbonyl; $Ni(CO)_4$ is more volatile, moreover, than $Co_2(CO)_8$, so that a high degree of separation of Ni and Co can be attained with distillation.

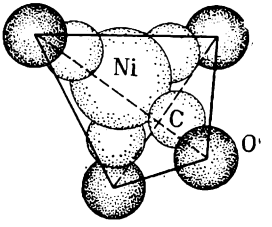


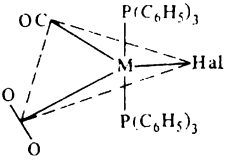
Fig. 238. Structure of the molecule of nickel tetracarbonyl $Ni(CO)_4$.

Carbonyls of Pd and Pt have not been obtained. Liquid $Ni(PF_3)_4$ and $Pd(PF_3)_4$ are known.

Complex cyanides $K_4[Ni(CN)_4]$ and $K_4[Pd(CN)_4]$ have been obtained for Ni(0) and Pd(0)—copper-red and yellowish solids (respectively) obtained by reducing $K_4[E(CN)_4]$ by potassium in liquid ammonia. They are powerful reducing agents displacing hydrogen, for example, from water

$$K_4[E(CN)_4] + 2H_2O = K_2[E(CN)_4] + 2KOH + H_2$$

Complexes are known for Group VIII *d* elements (with an electron configuration of d^8-d^{10}) in which the O_2 oxygen molecule acts as a ligand, e.g. $M(O_2)[P(C_6H_5)_3]_2$ (in which M = Ni, Pd, Pt) and $M(O_2)Hal(CO)[P(C_6H_5)_3]_2$ (in which M = Ir, Rh, Hal = Cl, Br, I).



The oxygen molecule is attached through $M—O_2$ donor-acceptor and dative interactions with involving the σ_z, π, and π^* orbitals of the O_2 molecule.

The oxygenyl compounds are good transmitters of oxygen and catalysts. Because of the activation of O_2, they are effective oxidants even in normal conditions. $M[P(C_6H_5)_3]_4$, for example, absorbs oxygen

$$M[P(C_6H_5)_3]_4 + O_2 = M(O_2)[P(C_6H_5)_3]_2 + 2P(C_6H_5)_3$$

while the $M(O_2)$ $[P(C_6H_5)_3]_2$ formed is an oxidant, e.g.

$$\overset{0}{Pt}(O_2)[P(C_6H_5)_3]_2 + NO_2 = \overset{2}{Pt}(NO_3)_2[Pt(C_6H_5)_3]_2$$

yielding hydrogen peroxide during hydrolysis.

Study of the formation and properties of oxygenyl, nitrogenyl, and like complexes is very important for the theory of catalysis. The catalytic functions of complex compounds can be explained as follows. An intermediate compound

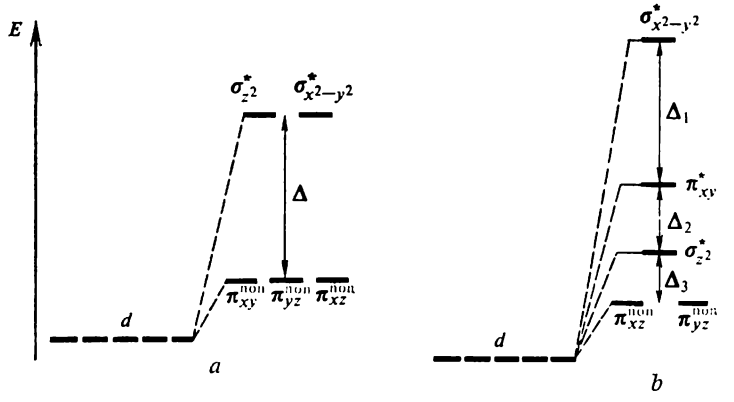


Fig. 239. The order of the molecular orbitals arising from *d* orbitals of the central atom in (*a*) octahedral and (*b*) planar square complexes

is formed first by the inclusion of a corresponding ligand L in the inner sphere of the complex (often with alteration of the complexing agent's coordination number). Because of the M—L interaction, the system's electron levels are then displaces and loosened. In oxygenyl complexes, for example, the internuclear distance O—O increases to between 0.13 and 0.16 nm (against the 0.121 nm in a free O_2 molecule). In this state, the incorporated molecule easier undergoes the next step of the reaction.

The activation of molecular oxygen through complexation is of great biochemical importance. A classical example is the combination of oxygen with haemoglobin.

Compounds of nickel(II), palladium(II), and platinum (II). Despite the similar electron configuration of the Ni^{2+}, Pd^{2+}, and Pt^{2+} (d^8) ions most Ni complexes have an octahedral structure, while planar square complexes are typical of Pd(II) and Pt(II).

The octahedral complexes of Ni(II) are paramagnetic, while the planar square complexes of Pd(II) and Pt(II) are diamagnetic. These

differences are due to essentially different splitting parameters: for Pd^{2+} and Pt^{2+} (*d* elements of the 5th and 6th periods) Δ is much higher than for Ni^{2+}, an element of the 4th period.

With high values of Δ, two electrons in the octahedral complex are in strongly antibonding molecular σ_d^* orbitals. Loss of these electrons, and the transition of Pd(II) and Pt(II) into metals with a +4 oxidation state, or transformation of the octahedral complex into a planar square one, are therefore more advantageous as regards energy. The distribution of electrons in the molecular orbitals arising through splitting of the *d* orbitals of Pd and Pt in octahedral and planar square complexes is shown in Fig. 239, which shows that a distribution of eight electrons in the orbitals of a planar square complex is more advantageous than in the molecular orbitals of an octahedral complex. The concentration of eight electrons in four molecular orbitals accounts for the diamagnetism of planar square complexes.

The diamagnetic ion $[Ni(CN)_4]^{2-}$ of nickel(II) has a planar square structure, owing to the high value of Δ, which in this case is due to the strong-field ligand CN^-.

Tetrahedral complexes of nickel(II) are rare (e.g. $[NiCl_4]^{2-}$, $[NiBr_4]^{2-}$).

Compounds of Ni(II), Pd(II), and Pt(II) are intensely coloured. Crystals of the binary compounds of Ni(II) more often have a coordination number of six;

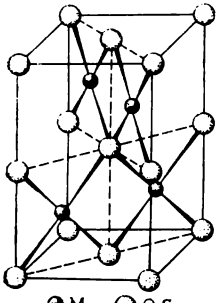


Fig. 240. The structure of PdO and PtO, PdS and PtS

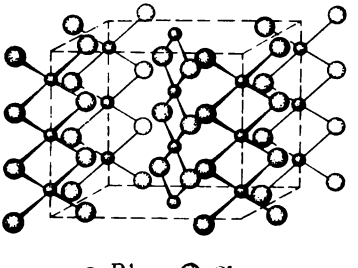
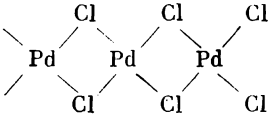


Fig. 241. The structure of $PdCl_2$

NiO, for instance, has a structure of NaCl type, NiF_2 has a rutile structure, and $NiCl_2$, $NiBr_2$, NiI_2, and $Ni(OH)_2$ have the layer structure shown in Fig. 232, and so on. Thus, Ni with a +2 oxidation state is like most of the other *d* elements of the 4th period in the structure of similar compounds.

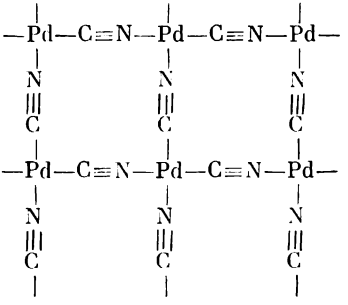
The unit cell of Pd(II) and Pt(II) compounds is a square. In the crystals of PdO and PtO, for instance (Fig. 240), the atoms of palladium and platinum are surrounded by four oxygen atoms at the apexes of the square, $d_{PdO} = 0.201$ nm, $d_{PtO} = 0.202$ nm. These squares are joined at their edges in chains that cross at an angle of 90°. PdS and PtS have similar structures.

The crystals of $PdCl_2$ (Fig. 241) have a chain structure with $PdCl_4$ square unit cells:



Platinum dichloride $PtCl_2$ has a quite different structure. Its redish-black crystals consist of octahedral Pt_6Cl_{12} clusters (see Fig. 229). Unlike $PdCl_2$, platinum dichloride is not soluble in water but is so in hydrochloric acid. It is supposed that platinum forms clusters (and palladium do not) because of the great difference in their sublimation (atomisation) energies (556 kJ/mol for platinum and 381 kJ/mol for palladium).

The dicyanides of palladium $Pd(CN)_2$ and nickel $Ni(CN)_2$ are polymers with a network structure (with a square unit cell):



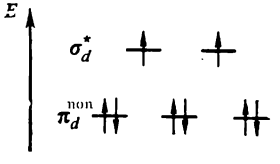
The oxide and hydroxide of nickel(II) are green. NiO is obtained by thermal decomposition of the hydroxide, carbonate, or nitrate of Ni(II). The hydroxide $Ni(OH)_2$ is formed by the action of alkalis on solutions of Ni(II) compounds. It precipitates as a bulky green gel that gradually crystallises on standing. NiO and $Ni(OH)_2$ are insoluble in water but react with acids.

The oxides and hydroxides of Pd(II) and Pt(II) are black solids, insoluble in water. PtO is also stable under the action of acids.

The ES sulphides of Ni(II) and its analogues are black substances precipitated by hydrogen sulphide from solutions of E(II) compounds. Fresh NiS is soluble in acids, but PdS and PtS are not. In contrast to Pd(II), and especially, to Pt(II), salts of oxy acids are characteristic of Ni(II).

Stable cation complexes of Ni(II) are octahedral hexa-aquo- and hexa-ammino complexes having the following electron configuration:

$$[\sigma]^{12}[\pi_d^{non}]^6[\sigma^*]^2$$



The aquo complex $[Ni(OH_2)_6]^{2+}$ is bright green (Δ 101 kJ/mol). It is formed by the dissolution of Ni(II) salts in water or by dissolving Ni, NiO, or $Ni(OH)_2$ in acids. Greens of various shades are also characteristic of the hexa-aquo crystal hydrates $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, $NiSnCl_6 \cdot 6H_2O$, and also of $NiSO_4 \cdot 7H_2O$, $K_2Ni(SO_4)_2 \cdot 6H_2O$, etc.

Structural studies show that the hexahydrates of Ni(II) $NiX_2 \cdot 6H_2O$ can be divided into two groups, one comprising compounds in which all six water molecules are in the inner sphere of the complex ion $[Ni(OH_2)_6]X_2$ (where X = $= NO_3^-$, ClO_3^-, BrO_3^-, ClO_4^- or 2X = SO_4^{2-}, SO_3^{2-}, SiF_6^{2-}, etc.), and the second embracing crystal hydrates in which an octahedral coordination of the Ni atom is created by two X atoms (Cl and Br) and four water molecules $[Ni(OH_2)_4X_2] \times \times 2H_2O$. The remaining two water molecules link the molecules of $[Ni(OH_2)_4X_2]$. The structure of $CoCl_2 \cdot 6H_2O$ is the same.

The structure of $NiCl_2 \cdot 4H_2O$ is of special interest. This crystal hydrate is a hexachloronickelate(II) of hexa-aquo nickel(II) $[Ni(OH_2)_6]_2[NiCl_6]$.

The crystals of $NiCl_2 \cdot 2H_2O$ and $NiBr_2 \cdot 2H_2O$ have a chain structure of the $CdCl_2 \cdot 2H_3N$ type.

The anhydrous salts of Ni(II), e.g. NiF_2, $NiCl_2$, $NiSO_4$, $Ni(CN)_2$, $Ni(NO_3)_2$, are usually a yellow of various shades. NiI_2 is black.

In contrast to the bright green $[Ni(OH_2)_6]^{2+}$, the ammino complex $[Ni(NH_3)_6]^{2+}$ (Δ = 129 kJ/mol) is intensely blue. Ammoniates, for example, are easily formed ($K_{st} = 1 \cdot 10^8$) by the interaction of solid $NiCl_2$ and ammonia

$$NiCl_2\,(c) + 6H_3N\,(g) \rightarrow [Ni(NH_3)_6]Cl_2(c)$$

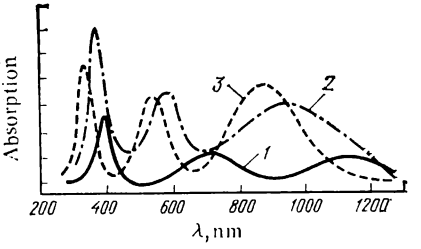


Fig. 242. Electron absorption spectra of (*1*) $[Ni(OH_2)_6]^{2+}$, (*2*) $[Ni(NH_3)_6]^{2+}$, and (*3*) $[Ni(en)_3]^{2+}$ ions

In addition to $[Ni(OH_2)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$, mixed $[Ni(OH_2)_{6-n}(NH_3)_n]^{2+}$ aquo-ammino complexes are also possible, where n is from 1 to 6. The substitution of H_2O by H_3N ligands alters the colour of the complexes from bright green to blue, owing to the increasing value of Δ (changes in the energy of d—d transitions), which shifts the absorption bands to shorter wavelengths (Fig. 242). The shift is even greater with ethylenediamine complexes $[Ni(en)_3]^{2+}$ (Δ = 134 kJ/mol), which are deep blue.

$Ni(OH)_2$ is easily soluble in the presence of ammonia and its salts because of the formation of ammoniates

$$Ni(OH)_2 + 6H_3N = [Ni(NH_3)_6](OH)_2$$

This reaction is employed in hydrometallurgy to extract nickel from ores.

A tetra-aquo ion $[Pd(OH_2)_4]^{2+}$, and several reddish-brown crystal hydrates $Pd(ClO_4)_2 \cdot 4H_2O$, $PdCl_2 \cdot 2H_2O$, $Pd(NO_3)_2 \cdot 2H_2O$, and

$PdSO_4 \cdot 2H_2O$, are known for palladium(II). For platinum(II) aquo complexes and the salts of oxy acids are unstable. The ammino complexes $[E(NH_3)_4]^{2+}$ of platinum(II) and palladium(II) are very stable and easily formed. They are *cation* complexes:

$$PdCl_2 + 4H_3N = [Pd(NH_3)_4]Cl_2$$

Many derivatives of cation complexes of Ni(II), Pd(II) and Pt(II) with organic ligands are also known.

Yellow $[Ni(CN)_4]^{2-}$ ($K_{st} = 3 \times 10^{31}$) is the most stable *anion* complex of Ni(II). Its derivatives are formed by the action of basic cyanides on compounds of Ni(II). Insoluble in water $Ni(CN)_2$ is first formed, which is then dissolved in an excess of basic cyanide

$$NiSO_4 + 2KCN = Ni(CN)_2 + K_2SO_4$$
$$Ni(CN)_2 + 2KCN = K_2[Ni(CN)_4]$$

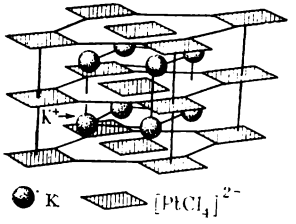


Fig. 243. The structure of $K_2[PtCl_4]$

The tetracyanide palladate(II) $[Pd(CN)_4]^{2-}$ and tetracyanide platinate(II) $[Pt(CN)_4]^{2-}$ ions are even more stable (the latter ion having a stability constant $K_{st} = 1 \cdot 10^{41}$). $H_2[Pt(CN)_4] \cdot 3H_2O$ is also known: its aqueous solution is the strong dibasic, *cyanoplatinic* acid.

Nickelates(II) of the type of $\overset{+1}{M}_4[NiHal_6]$, $\overset{+1}{M}_4[Ni(CNS)_6]$, etc. are quite easily formed. They are decomposed in water.

In contrast to nickelates(II), palladates(II) and platinates(II) are more varied and stable. The complex halides of Pd(II) and Pt(II), for example, have the following stability constants:

Ion	$[PdCl_4]^{2-}$	$[PdBr_4]^{2-}$	$[PdI_4]^{2-}$	$[PtCl_4]^{2-}$	$[PtBr_4]^{2-}$	$[PtI_4]^{2-}$
$\log K_{st}$	15.5	13.1	~ 25	16.0	20.5	~ 30

The increase in the stability of the complex ions in the series of $Cl^- - Br^- - I^-$ derivatives can be explained by the increasing role of the $E \rightarrow Hal$ π dative interaction, which increases with the size of free *d* orbitals of the Hal^- ions. The increasing $E \rightarrow X$ π dative interaction (along with the increasing mobility of the *d* electron pairs of the central atom) can also explain the increasing stability of the halide and cyanide complexes in the transition from Pd(II) to Pt(II).

Red $\overset{+1}{M}_2[ECl_4]$ salts are formed by the interaction of Pd(II) and Pt(II) compounds and corresponding salts of the alkali metals in hydrochloric acid. Water-soluble $K_2[PtCl_4]$ and $Na_2[PtCl_4]$ are the most important ones (Fig. 243), being used in the synthesis of various platinum compounds. Palladium compounds are usually synthesised from $PdCl_2 \cdot 2H_2O$.

Compounds in which Pd(II) and Pt(II) are simultaneously parts of a cation and an anion are also known, for example, $[Pt(NH_3)_4][PtCl_4]$, a green compound precipitated by mixing solutions of $[Pt(NH_3)_4]Cl_2$ and $K_2[PtCl_4]$:

$$[Pt(NH_3)_4]Cl_2 + K_2[PtCl_4] = [Pt(NH_3)_4][PtCl_4] + 2KCl$$

Red $[Pd(NH_3)_4][PdCl_4]$ has also been obtained.

Apart from the cation and anion complexes, there are also many varied neutral complexes of Pd(II) and Pt(II) with an $[E(NH_3)_4X_2]$ formula, in which $X = Cl^-$, Br^-, or NO_2^-. Geometrical (*cis-trans*) isomerism is characteristic of them. The composition $[Pt(NH_3)_2Cl_2]$, for example, corresponds to two compounds of differing properties, in particular of different colour, the *cis*-isomer being orange yellow, and the *trans*-isomer pale yellow. In contrast to the *trans*-isomer, the *cis*-isomer has a clearly marked anti-cancer physiological action.

These isomers are obtained by substantially different methods, the *cis*-isomer by the replacement of two chloride ions by ammonia molecules in the tetrachloroplatinate(II) complex:

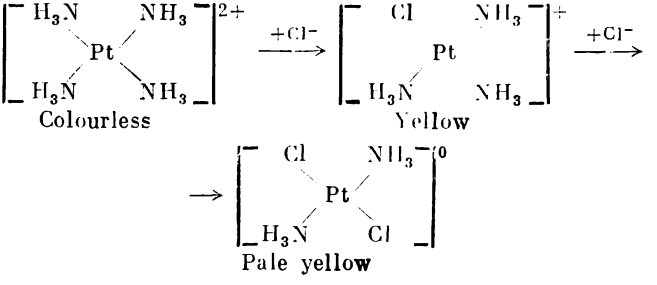
$$K_2[PtCl_4] + 2H_3N = \underset{\textit{cis}\text{-Isomer}}{[Pt(NH_3)_2Cl_2]} + 2KCl$$

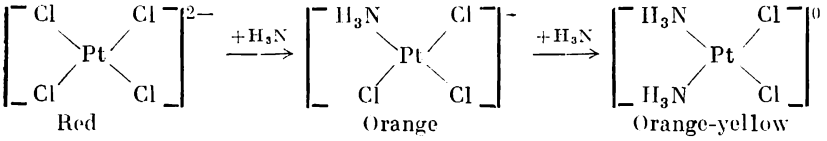
and the *trans*-isomer by the displacement of two ammonia molecules to the chloride ion in the tetra-amine-platinum(II) complex:

$$[Pt(NH_3)_4]Cl_2 + 2HCl = \underset{\textit{trans}\text{-Isomer}}{[Pt(NH_3)_2Cl_2]} + 2NH_4Cl$$

The principle of *trans effect* established by Chernyaev (1926), according to which certain ligands facilitate the substitution of ligands that are in a *trans* position to them, is very important for understanding the direction that reaction will take when ligands are substituted in complexes. It has been established experimentally that the *trans* effect of ligands increases for compounds of platinum(II) in the series $H_2O < H_3N < OH^- < Cl^- < Br^- < CNS^-$, $I^- < NO_2^- < CO$, CN^-.

The reactions above used for obtaining *cis*- and *trans*-isomers of $[Pt(NH_3)_2Cl_2]$ can be explained by different *trans* effects of H_3N and Cl^-:





Red Orange Orange-yellow

Since the *trans* effect of Cl^- is more marked than that of H_3N, the ligand in the *trans* position to Cl^- will be replaced in the second stage of this reaction. Starting with the $[Pt(NH_3)_4]^{2+}$ ion we can thus only obtain the *trans*-isomer, and starting with the $[PtCl_4]^{2-}$ ion only the *cis*-isomer. *Trans* effect has played an important role in development of the synthesis of complex compounds.

Compounds of nickel(IV), palladium(IV), and platinum(IV). An oxidation state of + 4 is characteristic of platinum. Few derivatives of Pd(IV) are oxidants. Compounds of Ni(IV) are even fewer in number and less stable. An oxide PtO_2 (various shades of brown), hydroxide $Pt(OH)_4$ (more exactly $PtO_2 \cdot nH_2O$), halides $PtHal_4$, sulphide PtS_2, and many derivatives of its cation, neutral, and anion complexes are known for platinum(IV).

The coordination number of Pd(IV) and Pt(IV) is six, which corresponds to an octahedral configuration of the complexes, which are diamagnetic, and have the following electron configuration:

$$[\sigma]^{12}\,[\pi_d^{non}]^6$$

Binary compounds of Pt(IV) are obtained by direct interaction of the simple substances at red-hot temperature, or by decomposing the corresponding complex compounds.

Acidic properties prevail over basic ones in binary compounds of Pd(IV) and Pt(IV). During dissolution of palladium(IV) or platinum(IV) hydroxide $EO_2 \cdot nH_2O$ anion complexes are formed in acids and alkalis, e.g.

$$Pd(OH)_4 + 2NaOH = Na_2[Pd(OH)_6]$$

$$Pt(OH)_4 + 6HCl = H_2[PtCl_6] + 4H_2O$$

Their variety can be judged from the following series of Pt(IV) derivatives:

$$[Pt(NH_3)_6]Cl_4,\quad [Pt(NH_3)_5Cl]Cl_3,\quad [Pt(NH_3)_4Cl_2]Cl_2,$$
$$[Pt(NH_3)_3Cl_3]Cl,\quad [Pt(NH_3)_2Cl_4],\quad K[Pt(NH_3)Cl_5],\quad K_2[PtCl_6]$$

The character of the coordination of the chloride ion in these compounds can be determined chemically. During the interaction of solutions of $[Pt(NH_3)_6]Cl_4$ and $AgNO_3$, four moles of AgCl are precipitated per mole of Pt. Three moles and two moles of AgCl are correspondingly precipitated from solutions of $[Pt(NH_3)_5Cl]Cl_3$ and $[Pt(NH_3)_4Cl_2]Cl_2$, while AgCl is precipitated only from $[Pt(NH_3)_2Cl_4]$ after long standing or when heated. The electrical

conductivity of the solutions changes in accordance with the character of the ionisation and, given equal molar concentrations, is highest in $[Pt(NH_3)_6]Cl_4$ and lowest in $[Pt(NH_3)_2Cl_4]$ (Fig. 244).

The ammoniates of Pt(IV), for example, are compounds with a $[Pt(NH_3)_6]Cl_4$, $[Pt(NH_3)_4Cl_2]Cl_2$, and $[Pt(NH_3)_2Cl_4]$ composition.

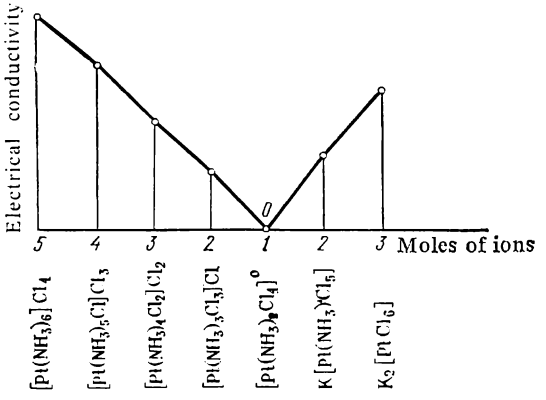


Fig. 244. Molar electrical conductivity of Pt(IV) compounds depending on their composition

The last two have a characteristic geometric isomerism: the *cis*-$[Pt(NH_3)_2Cl_4]$ is orange while the *trans*-$[Pt(NH_3)_2Cl_4]$ is yellow. The arrangement of the *trans*-complexes $[Pt(NH_3)_2Cl_4]$ in the crystal is shown in Fig. 245.

The formation of complexes of the $[PtHal_6]^{2-}$ type (where Hal = Cl, Br, and I) by the interaction of hydrohalic acids and basic halides is very typical of platinum tetrahalides:

$$2HCl + PtCl_4 = H_2[PtCl_6]$$

$$2NaCl + PtCl_4 = Na_2[PtCl_6]$$

The $[PtHal_6]^{2-}$ ions (except $[PtF_6]^{2-}$) are very stable. The interaction of $AgNO_3$ and solutions of hexachloroplatinates(IV), for instance, yields a pale brown precipitate $Ag_2[PtCl_6]$ (not AgCl). In contrast to $Na_2[PtCl_6]$, the hexachloroplatinates(IV) of K^+, Rb^+, Cs^+, and NH_4^+ are poorly soluble in water and precipitate as yellow solids, which is used to detect them in analytical chemistry. *Hexachloroplatinic acid* $H_2[PtCl_6] \cdot 6H_2O$ is a red-brown crystalline solid, that deliquesces in air and is readily soluble in water, alcohol, and ether. The acid is obtained by evaporating solutions of the products of the interaction

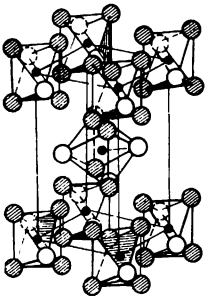


Fig. 245. The structure of the $[Pt(NH_3)_2Cl_4]$ crystal

of $PtCl_4$ and hydrochloric acid, or by dissolving platinum in aqua regia.

Apart from $[PtX_6]^{2-}$ (X = Cl^-, Br^-, I^-, CN^-, SCN^-, OH^-), there are many anion complexes with heterogeneous ligands, e.g. the series $\overset{+1}{M}_2[Pt(OH)_6]$, $\overset{+1}{M}_2[Pt(OH)_5Cl]$, $\overset{+1}{M}_2[Pt(OH)_4Cl_2]$, $\overset{+1}{M}_2[Pt(OH)_3Cl_3]$, $\overset{+1}{M}_2[Pt(OH)_2Cl_4]$, $\overset{+1}{M}_2[Pt(OH)Cl_5]$ and $\overset{+1}{M}_2[PtCl_6]$. Some of these can be obtained during hydrolysis of $PtCl_4$:

$$PtCl_4 + 2HOH = H_2[Pt(OH)_2Cl_4]$$

or by the action of alkalis on chloroplatinates(IV):

$$Na_2[PtCl_6] + 6NaOH = Na_2[Pt(OH)_6] + 6NaCl$$

Compounds of nickel(IV) can be prepared by oxidising nickel(II) fluoride by xenon fluoride in the presence of a basic fluoride:

$$\overset{+2}{Ni}F_2 + 2CsF + XeF_2 = Cs_2\overset{+4}{Ni}F_6 + Xe$$

Compounds of platinum(VI). Like other 5*d* elements, platinum forms a hexafluoride PtF_6, which is a dark red, volatile crystalline solid (m.p. 61 °C, b.p. 69 °C) obtained by burning platinum in a fluorine atmosphere. The stability of hexafluorides decreases in the series $WF_6 > ReF_6 > OsF_6 > IrF_6 > PtF_6$. PtF_6 is especially unstable, and is one of the strongest oxidants (electron affinity, 7 eV). It is the strongest fluorinating agent known, readily fluorinating BrF_3 to BrF_5, reacts vigorously with metallic uranium to form UF_6, decomposes water with liberation of oxygen, and reacts with glass. Platinum hexafluoride also oxidises molecular oxygen to $O_2^+[PtF_6]^-$. Since the first ionisation potential of molecular oxygen $O_2 \rightarrow O_2^+$ is 12.08 V, i.e. higher than with xenon (12.13 V), it was suggested that $Xe^+[PtF_6]^-$ could be formed:

$$Xe + PtF_6 = Xe^+[PtF_6]^-$$

The compound was actually obtained soon afterward. It is an orange, crystalline solid, stable at 20 °C, that sublimes in vacuum without decomposition. Its synthesis was the first step in broad research that led to the development of methods for obtaining various compounds of the noble gases.

7.7. The Refining of Platinum Metals

The bulk of the platinum metals obtained is recovered from the anode sludge formed during the electrorefining of nickel and copper. The platinum metals are separated (*affinage*) from one another by a complicated chemical treatment consisting of the following stages:

1. The anode sludge is concentrated and then heated with aqua regia. Pt, Pd, Rh, Ir and Ru are dissolved as $H_2[PtCl_6]$, $H_2[PdCl_4]$,

$H_3[RhCl_6]$, $H_2[IrCl_6]$, and $H_2[RuCl_6]$, while Os remains undissolved together with the insoluble mineral residue.

2. NH_4Cl is added to the solution obtained to precipitate first $(NH_4)_2[PtCl_6]$, and then $(NH_4)_2[IrCl_6]$ and $(NH_4)_2[RuCl_6]$. After a series of operations, $[Pd(NH_3)_2Cl_2]$ and $[Rh(NH_3)_3Cl_3]$ are precipitated by H_3N. The undissolved residue is fused with BaO_2. The OsO_4 formed during this operation is distilled. Ruthenium and iridium are separated in a similar way.

3. When the compounds obtained are calcined in a reducing atmosphere (often in the presence of hydrogen), the free metals are obtained.

Platinum metals of high purity are refined by repeated dissolution, precipitation, and decomposition of the corresponding compounds.

Separation on ion-exchange resins has become very important in recent years for obtaining pure platinum metals.

CHAPTER 8

Group I *d* Elements

Copper Cu, silver Ag, and gold Au are the next-to-last *d* elements in their periods, so there should be nine electrons in the $(n-1)\,d$ state in their atoms, but because of stability of the d^{10} configuration it is more advantageous for one *s* electron to pass to the $(n-1)\,d$ state, so that Cu, Ag, and Au have one electron in the *s* state in the outer shell and 18 electrons each ($s^2p^6d^{10}$) in the penultimate one. Their main characteristics are as follows:

	$_{29}Cu$	$_{47}Ag$	$_{79}Au$
Atomic mass	63.62	107.87	196.97
Valence electrons	$3d^{10}4s^1$	$4d^{10}5s^1$	$5d^{10}6s^1$
Metallic atom radius, nm	0.128	0.144	0.144
Ion E^+ radius, nm	0.098	0.113	0.137
Ionisation energy, eV			
$E^0 \rightarrow E^+$	7.726	7.576	9.226
$E^+ \rightarrow E^{2+}$	20.29	21.49	20.5
$E^{2+} \rightarrow E^{3+}$	36.8	34.8	43.5
Electron affinity, eV	1.2	1.3	2.3
Abundance, mole per cent	3.6×10^{-3}	1.6×10^{-6}	5×10^{-8}
Natural isotopes	^{63}Cu (69.1%) ^{65}Cu (30.9%)	^{107}Ag (51.35%) ^{109}Ag (48.65%)	^{197}Au (100%)

First ionisation energies of the elements in the copper subgroup are much higher than those of group I *s* elements, which is due to penetration of the outer *ns* electron through the screen of $(n-1)\,d^{10}$ electrons. The first ionisation energy falls in the transition from Cu to Ag because of the higher principal quantum number *n*, while

there is a further increase in the ionisation energy of Au owing to penetration of the 6*s* electron not only through the $5d^{10}$ electron screen but also through the screen of $4f^{14}$ electrons. The second ionisation energy (removal of an electron from the $(n-1)\,d^{10}$ subshell), is almost the same for all three elements and is much lower than with the alkali metals.

In accordance with what we have said, the elements of the copper subgroup display +2 and +3 oxidation states as well as a +1 oxidation one. The most characteristic oxidation state of copper is +2, of gold +3, and of silver +1. The special stability of silver's +1 oxidation state is due to the relatively higher strength of the $4d^{10}$ configuration, since it is already found in palladium (which comes before silver in the periodic system). Compounds of gold(V) are known.

Electron affinity, it is interesting to note, is much higher in Cu, Ag, and Au not only than in Group I *s* elements but also in oxygen and sulphur, which is also connected with penetration of *s* electrons of the outer shell closer to the nucleus.

All this accounts for the greater tendency of copper and its analogues (than the alkali metals) to form covalent bonds.

The peculiarity of the electron structure of the atoms of copper subgroup accounts for the relatively higher stability of the diatomic molecules Cu_2, Ag_2, and Au_2 (dissociation energy 174, 158, and 210 kJ/mol respectively) than that of K_2, Rb_2, and Cs_2 (dissociation energy of the order of 40 kJ/mol). The strength of Cu_2, Ag_2, and Au_2 molecules is due to additional π bonding through free *np* orbitals and $(n-1)d$ electron pairs.

Table 55. **Oxidation States and Spatial Configuration of Complexes (Unit Cells) of the Copper Subgroup Elements**

Oxidation state	Electron configuration	Coordination number	Spatial configuration	Typical compounds
+1	d^{10}	2	Linear	Cu_2O, Ag_2O, AgCN, AgCNS, AuI, $[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
		3	Planar triangle	$K[Cu(CN)_2]$
		4	Tetrahedral	CuHal, $[Cu(CN)_4]^{3-}$, $[Ag(CNS)_4]^{3-}$
		6	Octahedral	AgHal
+2	d^9	4	Square	CuO, $CuCl_2$
		6	Distorted octahedral	$CuCl_2 \cdot 2H_2O$, $[Cu(NH_3)_4(OH_2)_2]^{2+}$, $(NH_4)_2[CuCl_4]$
+3	d^8	4	Square	$AuHal_3$, $[AuHal_4]^-$, $Cs[CuCl_4]$, $KCuO_2$

The elements of the copper subgroup can form both cation and anion complexes. As the oxidisation state rises, there is understandably a greater tendency to form anion complexes. The oxidation states of elements of the subgroup and the corresponding coordination numbers and spatial configurations of complexes are given in Table 55.

8.1. The Copper Subgroup

The most important of the natural compounds of copper are *copper pyrite* (*chalcopyrite*) $CuFeS_2$, *copper glance* Cu_2S, and also *cuprite* Cu_2O, *malachite* $CuCO_3 \cdot Cu(OH)_2$, etc. Silver occurs in the sulphide minerals of other metals (Pb, Zn, Cd, etc.). Cu, Ag, and Au are also quite common in arsenide, stibide, and sulphide-arsenide minerals. Copper, silver, and especially gold, also occur in the native state.

The simple substances. Copper, silver, and gold are red, white, and yellow metals respectively, with face-centred cubic lattice. Since both *ns* and $(n-1)d$ electrons are involved in the formation of bonds in copper and its analogues, their heats of sublimation and melting points being much higher than those of the alkali metals. Copper, silver, and gold are exceptionally malleable (especially gold); they are also better conductors of electricity and heat than the other metals. Certain of their constants are as follows:

	Cu	Ag	Au
Density, g/cm³	8.96	10.50	19.3
Hardness (diamond = 10)	3.0	2.7	2.5
S°, J·K·mol	33.5	42.55	47.4
Electrical conductivity	57	59	40
Thermal conductivity ($H_2O = 1$)	46	49	35
M.p., °C	1083	960.5	1063.4
B.p., °C	2543	2167	2880
$\Delta H^\circ_{subl.,\,298}$, kJ/mol	339.6	283.6	366.6
E°_{298}, V			
$E^+ + 1e^- = E$	+0.52	+0.799	+1.69
$E^{2+} + 2e^- = E$	+0.34	—	—
$E^{3+} + 3e^- = E$	—	—	+1.498

The chemical activity of copper and its analogues is not high and decreases with increasing atomic number. This is also shown by the Gibbs' energies of formation of their binary compounds. The metals react most easily with the halogens: copper at normal temperature, and silver and gold when heated.

Compound	CuCl (c)	AgCl (c)	AuCl (c)	$CuCl_2$ (c)	$AuCl_3$ (c)
$\Delta G^\circ_{f,\,298}$, kJ/mol	−120	−110	−18	−171	−54

Only copper reacts directly with oxygen, forming CuO at red-hot temperature and Cu_2O at higher ones. Copper and silver react di

rectly with sulphur:

Compound	Cu_2O (c)	Ag_2O (c)	CuO (c)	Au_2O_3 (c)	Cu_2S (c)	Ag_2S (c)
$\Delta G^\circ_{f,298}$, kJ/mol	—151	—11	—129	+79	—86	—47

When exposed to air copper becomes covered with a dense greyish-green film of basic carbonates. If there is hydrogen sulphide in the air, silver also becomes coated with a black film of Ag_2S. Copper and its analogues do not react with hydrogen.

The diminishing chemical activity in the Cu—Ag—Au series is also shown by the standard potentials. Since copper, silver, and gold come after hydrogen in the electromotive series, they can only be oxidised by acids through the anion: Cu and Ag are soluble in HNO_3 and in concentrated H_2SO_4, and Au in hot concentrated H_2SeO_4. The best solvents for gold are HCl saturated with chlorine, and aqua regia. In both cases gold is dissolved through oxidation by atomic chlorine and the formation of an anion complex:

$$Au + HNO_3 + 4HCl = H[AuCl_4] + NO + 2H_2O$$
$$Au + 3Cl + HCl = H[AuCl_4]$$

Cu, Ag, and Au are stable in alkalis in the absence of oxidants.

Copper and its analogues dissolve in solutions of basic cyanides in the presence of oxygen, e.g.

$$4Au + O_2 + 8CN^- + 2H_2O = 4[Au(CN)_2]^- + 4OH^-$$

Copper, in addition, is soluble in aqueous solutions of ammonia in the presence of oxygen:

$$4Cu + O_2 + 8H_3N + 2H_2O = 4[Cu(NH_3)_2]^+ + 4OH^-$$

Copper, silver, and gold form alloys with each other and with other metals. The most important copper alloys are *bronzes* (90 per cent Cu, 10 per cent Sn), *tombac* (90 per cent Cu, 10 per cent Zn), *Melchior* (68 per cent Cu, 30 per cent Ni, 1 per cent Mn, 1 per cent Fe), *brass* (60 per cent Cu, 40 per cent Zn), *German silver* (65 per cent Cu, 20 per cent Zn, 15 per cent Ni), and also coin alloys (95 per cent Cu and 5 per cent Al for 'copper' coins, and 80 per cent Cu and 20 per cent Ni for 'silver' ones).

Copper is refined by pyrometallurgical techniques, less frequently by hydrometallurgical methods. The pyrometallurgical process consists in partial oxidation of the sulphide ores to copper oxides, which are then reduced, reacting with excess sulphide:

$$2Cu_2O + Cu_2S = 6Cu + SO_2$$

The pyrometallurgical process of extracting copper from sulphide ores of the type of $CuFeS_2$ can be described by the following summary equation:

$$2CuFeS_2 + 5O_2 + 2SiO_2 = 2Cu + 2FeSiO_3 + 4SO_2$$

To separate copper from the iron and gangue, the ore is roasted in air, and the iron sulphides are converted into FeO, with liberation of SO_2. The roasted ore is then mixed with silica and coke, and the mixture is melted. As a result, two liquid layers are formed, a supernatant one that is an alloy of the oxides and silicates (*slag*) containing some iron (as $FeSiO_3$) and the gangue constituents, and a lower layer, an alloy of the sulphides (known as *matte*), containing copper (mainly as $Cu_2S \cdot FeS$) and the accompanying valuable metals (Au, Ag, Se, Te, Ni, etc.). The liquid matte is then oxidised by blowing compressed air through it to burn out the remaining sulphur and iron, and to recover metallic copper

$$2(Cu_2S \cdot FeS) + 5O_2 + 2SiO_2 = 4Cu + 2FeSiO_3 + 4SO_2$$

The SO_2 produced in the pyrometallurgical treatment of ores is used to make sulphuric acid, while the slag is employed to make slag wool, stonework, slag concrete, etc.

The blister copper produced by this process contains 95 to 98 per cent Cu. Copper of high purity is obtained by electrolysis of $CuSO_4$ with a copper anode. Noble metals like selenium and tellurium, and other valuable admixtures, are concentrated in the anode sludge, from which they are then recovered by special processing.

Hydrometallurgical methods of refining copper are based on selective dissolution of copper minerals, usually in dilute solutions of H_2SO_4 or ammonia. Copper is recovered from the solution thus obtained, either by displacement by iron or by electrolysis.

Native gold is separated from the dirt by washing with water, and then dissolving in liquid mercury with subsequent fractional distillation of the amalgam. The best method for separating gold from gangue is the cyanide method, which consists in dissolving Au in a solution of NaCN with oxidation by atmospheric oxygen and transition to a complex compound $Na[Au(CN)_2]$, with subsequent displacement from the cyanoaurate(I) by metallic zinc:

$$2Na[Au(CN)_2] + Zn = Na_2[Zn(CN)_4] + 2Au$$

8.2. Compounds of the Copper Subgroup Elements

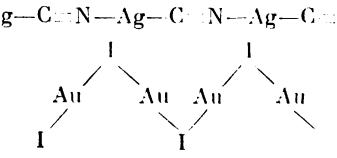
Compounds of copper(I), silver(I), and gold(I). Copper and its analogues in the +1 oxidation state correspond to the d^{10} electron configuration. It is supposed that the E^+ ions can act as both σ acceptors and π donors of electron pairs. The mobility of *d* electron pairs increases in the Cu(I)—Ag(I)—Au(I) series, which explains the increasing capacity of these elements for a π dative interaction.

As already said, the +1 oxidation state is most characteristic of silver; with copper and especially gold it occurs less frequently. In aqueous solutions, this oxidation state is stabilised mainly in the presence of ligands of a π acceptor type; for example, equilibrium is displaced in solution toward the formation of E(I) derivatives in the presence of, for example, CN^- and I^- ions:

$$2\overset{+1}{Cu}\ (sol) \rightleftarrows \overset{0}{Cu}\ (c) + \overset{+2}{Cu}\ (sol) \quad \text{and} \quad 3\overset{+1}{Au}\ (sol) \rightleftarrows 2\overset{0}{Au}\ (c) + \overset{+3}{Au}\ (sol)$$

The typical coordination numbers of copper(I) and its analogues are two and four; silver(I) also has a coordination number of six.

Crystals of AgCN, AgCNS, AuI and EN_3, for instance, are formed by chains of the type of



Crystals of Cu_2O and Ag_2O have linear-tetrahedral coordination of the atoms (Fig. 246); the coordination number of copper is four in the Cullal halides (sphalerite structure, see Fig. 194*a*), while the coordination number of silver in the halides AgHal is six (NaCl structure).

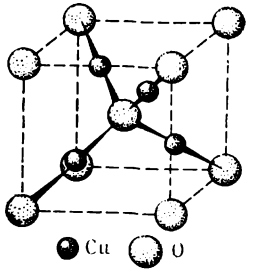


Fig. 246. The crystal structure of cuprite Cu_2O

Binary compounds of Cu(I), Ag(I), and Au(I) are solid, crystalline, salt-like substances, usually insoluble in water. The derivatives of silver(I) are formed by direct interaction of the simple substances, and those of Cu(I) and Au(I) by reduction of the corresponding compounds of Cu(II) and Au(III). Of the salts of oxy acids and E(I), the derivatives of silver (water-soluble $AgNO_3$, $AgClO_4$, $AgClO_3$ and barely soluble Ag_2SO_4, Ag_2CO_3, etc.) are relatively more stable.

The aquo complexes of E(I) are unstable and crystal hydrates are not characteristic, but the ammino complexes of Cu(I) and Ag(I) of the $[E(NH_3)_2]^+$ type are stable. Therefore most compounds of Cu(I) and Ag(I) are quite readily soluble in the presence of ammonia, for example:

$$CuCl + 2H_3N = [Cu(NH_3)_2]Cl$$

$$Ag_2O + 4H_3N + H_2O \quad 2[Ag(NH_3)_2](OH)$$

Hydroxides of the $[E(NH_3)_2](OH)$ type are much more stable than EOH and are comparable in strength with alkalis, owing to lowering of the polarising effect of the E^+ cation on OH^- ions, because of screening by the ammonia molecules.

The EOH hydroxides are unstable bases (for AgOH $K_b = 5.0 \times 10^{-3}$). Attempts to isolate them by exchange reactions end in liberation of the oxides Cu_2O (red) and Ag_2O (dark brown), e.g.

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$$

The acidic nature of E(I) binary compounds is seen during their reactions with the appropriate basic compounds, in which various cuprates(I), argentates(I), and aurates(I) are produced; E_2O, for

instance, are slightly soluble in strong alkaline solutions:

$$Cu_2O + 2NaOH + H_2O = 2Na[Cu(OH)_2]$$

The EHal halides are insoluble in water and acids, but are quite soluble in strong solutions of hydrohalic acids or basic halides

$$CuCl + HCl = H[CuCl_2]$$

$$AgI + KI = K[AgI_2]$$

The water-insoluble ECN cyanides, E_2S sulphides, etc., behave in a similar way. Their most important reaction is the dissolution of silver halides in solutions of sodium thiosulphate:

$$AgBr + 2Na_2S_2O_3 = Na_3[Ag(S_2O_3)_2] + NaBr$$

which takes place during the fixing of photographs with 'hypo'.

Most compounds of copper(I) and gold(I) are easily oxidised (even by the molecular oxygen of air) to corresponding stable derivatives of Cu(II) and Au(III), e.g.

$$4\overset{+1}{C}uCl\ (c) + O_2\ (g) + 4HCl\ (sol) = 4\overset{+2}{C}uCl_2\ (sol) + 2H_2O\ (l)$$

Disproportionation reactions are also characteristic of derivatives of Cu(I) and Au(I):

$$2\overset{+1}{C}uCl\ (c) = \overset{0}{C}u\ (c) + \overset{+2}{C}uCl_2\ (sol)$$

$$3\overset{+1}{A}uCl(c) + KCl\ (sol) = K[\overset{+3}{A}uCl_4]\ (sol) + 2\overset{0}{A}u\ (c)$$

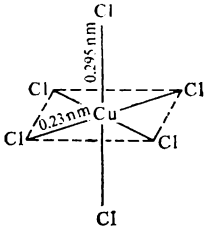
Most E(I) compounds are easily decomposed by the action of light or heat, and are therefore stored in dark glass jars. The high sensitivity of silver halides to light is utilised in light-sensitive emulsions. $AgNO_3$, from which all other silver compounds are obtained, is most important. The copper(I) oxide is used to stain glass and enamels, and is also employed in semiconductor engineering.

Compounds of copper(II). The oxidation state +2 is characteristic of copper alone. The maximum coordination number of Cu(II) is six, which corresponds to octahedral complexes (unit cells) of the following electron configuration

$$[\sigma]^{12}\,[\pi_d^{non}]^6\,[\sigma_{z^2}^*]^2\,[\sigma_{x^2-y^2}^*]^1$$

Since there is only one electron in the $\sigma_{x^2-y^2}^*$ orbital, in contrast to the $\sigma_{z^2}^*$ orbital, the Cu—L bond formed by the $\sigma_{x^2-y^2}$ electrons is stronger than that formed by the σ_{z^2} electrons. In other words, the four ligands in the *xy* plane are more strongly bound to Cu than the two ligands on the *z* axis. The distance between the copper atoms and

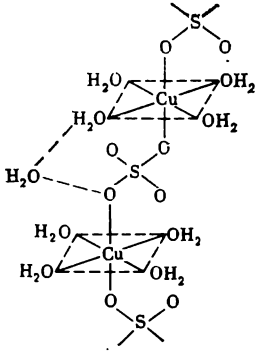
the ligands in the *xy* plane is therefore shorter than that between Cu and the ligands on the *z* axis, e.g. in the crystal of $CuCl_2$



The difference is occasionally so great that complexes of Cu(II) can be regarded as square. Compounds are thus most frequently met in which copper's coordination number is four (square) and six (distorted octahedron).

Cation and anion complexes are characteristic of copper(II). When its salts are dissolved in water, or when black CuO or blue $Cu(OH)_2$ reacts with acids, blue aquo complexes of the type of $[Cu(OH_2)_6]^{2+}$ are formed. Most of the crystal hydrates, e.g. $Cu(NO_3)_2 \cdot 6H_2O$, are similarly coloured.

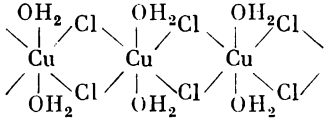
Four molecules of water are coordinated in the plane around Cu(II) in blue vitriol $CuSO_4 \cdot 5H_2O$ and two SO_4^{2-} groups along the axis. The fifth water molecule acts as a bridge connecting a water molecule in the plane and an SO_4^{2-} group by means of a hydrogen bond:



Some of the water molecules in the other crystal hydrates (with an odd number of water molecules, e.g. in $NiSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$) also act as bridges.

Green and dark brown crystal hydrates of Cu(II) are also met. In them, the anions also act as ligands, in addition to the water molecules. Thus the copper atom in green $CuCl_2 \cdot 2H_2O$ is surrounded by

two molecules of water and four atoms of chlorine:



When water is added to $CuCl_2 \cdot 2H_2O$, its colour changes to blue, i.e. a $[Cu(OH_2)_6]^{2+}$ aquo complex is formed.

The hydrolysis of Cu(II) salts is often accompanied with the formation of barely soluble compounds $Cu(NO_3)_2 \cdot 3Cu(OH)_2$, $CuSO_4 \cdot 2Cu(OH)_2$ and $CuCl_2 \cdot 3Cu(OH)_2$ (basic salts), which should be regarded as derivatives of -ol cation complexes. Most of them occur as minerals.

Of the other cation complexes of copper(II) those with nitrogen-containing ligands are very characteristic, e.g. $[Cu(NH_3)_4(OH_2)_2]^{2+}$ ($K_{st} = 1 \times 10^{12}$) and the chelate complex $[Cu(en)_2(OH_2)_2]^{2+}$ ($K_{st} = 1 \times 10^{20}$). The formation of ammoniates, in particular, explains the solubility of $Cu(OH)_2$ in aqueous solutions of ammonia:

$$Cu(OH)_2\ (s) + 4H_3N\ (sol) + 2H_2O\ (l) = [Cu(NH_3)_4(OH_2)_2](OH)_2\ (sol)$$

The substitution of nitrogen-containing ligands for the water molecules in the aquo complex $[Cu(OH_2)_6]^{2+}$ intensifies the blue colour:

$$\underset{\text{Blue}}{[Cu(OH_2)_6]^{2+}} \quad \underset{\text{Dark blue}}{[Cu(NH_3)_4(OH_2)_2]^{2+}} \quad \underset{\text{Intense dark blue}}{[Cu(en)_2(OH_2)_2]^{2+}}$$

The variation of colour is due to strengthening of the ligand field in the series OH_2—NH_3— en, which shifts the absorption band from the far red to the middle red region of the spectrum. (Maximum absorption of the $[Cu(OH_2)_6]^{2+}$ ion is at around 800 nm, and of the $[Cu(NH_3)_4(OH_2)_2]^{2+}$ ion at approximately 600 nm.) On the other hand $CuSO_4$ is colourless, since the field of the SO_4^{2-} ion is so weak that the *d*—*d* transition corresponds to absorption in the infra-red region of the spectrum.

Cu(II) compounds are more stable in general than similar derivatives of Cu(I). Thus, $Cu(OH)_2$ breaks down into CuO and H_2O only when heated, CuF_2 and $CuCl_2$ begin to decompose into CuHal and HaI_2 at 950 °C and 500 °C respectively, while CuI_2 ($\Delta G^\circ_{f,\,298} = -8$ kJ/mol) decomposes at normal temperatures to give CuI ($\Delta G^\circ_{f,\,298} = -71$ kJ/mol). A redox reaction therefore occurs when it is attempted to obtain CuI_2 by an exchange reaction

$$2Cu^{2+}\ (sol) + 4I^-\ (sol) = 2CuI\ (s) + I_2\ (s)$$

$Cu(CN)_2$ and $Cu(CNS)_2$ decompose in a similar way:

$$2CuSO_4 + 4KCN = 2CuCN + (CN)_2 + 2K_2SO_4$$

Anion complexes, cuprates(II), are also characteristic of Cu(II). $Cu(OH)_2$ partially dissolves, for instance, when heated in concentrated solutions of alkalis, to form dark blue hydroxycuprates(II)

of the type of $\overset{+1}{M}_2[Cu(OH)_4]$, some of which have been isolated in the free state. Hydroxycuprates(II) are easily decomposed in aqueous solutions, which indicates that the properties of $Cu(OH)_2$ are weakly acidic.

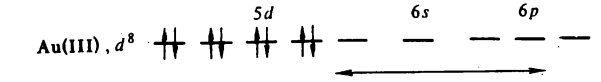
In the presence of an excess of basic halides, $CuHal_2$ form halogen cuprates(II) of the type of $\overset{+1}{M}[CuHal_3]$ and $\overset{+1}{M}_2[CuHal_4]$. Cyanocuprates(II) of the type of $\overset{+1}{M}_2[Cu(CN)_4]$, unlike $Cu(CN)_2$, are quite stable and readily soluble in water.

Anion complexes of Cu(II) with carbonate, sulphate, and other complex anions are also known. A dark blue potassium carbonatecuprate(II) $K_2[Cu(CO_3)_2]$, for instance, has been isolated, and $CuSO_4$ is crystallised as an $\overset{+1}{M}_2Cu(SO_4)_2 \cdot 6H_2O$ from solutions of the sulphates of alkali metals.

Of the derivatives of silver(II), AgF_2 and certain complex compounds with organic ligands are more or less stable. No compounds of gold(II) are known.

The most important copper(II) compound, commercially, is blue vitriol $CuSO_4 \cdot 5H_2O$, which is used in the making of mineral paints, to control pests and plant diseases in agriculture, as the initial material for obtaining copper and its compounds, and so on.

Compounds of copper(III), silver(III), and gold(III). The oxidation state +3 is most characteristic of gold. The diamagnetism of gold(III) compounds accords with the involvement of the $5d\,6s\,6p^2$ orbitals of the $Au^{3+}(d^8)$ ion in the formation of bonds:

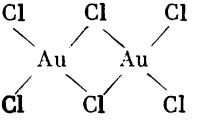


This corresponds to a square configuration of the complexes and unit cells of gold(III) compounds.

The following binary compounds of gold(III) are known:

Compound	Au_2O_3 (c) black-brown	AuF_3 (c) orange	$AuCl_3$ (c) red	$AuBr_3$ (c) dark-brown	Au_2S_3 (c) black	$Au(OH)_3$ (c) red-brown
$\Delta G^\circ_{f,\,298}$, kJ/mol	+79	−297	−54	−25	—	−350

Only $AuCl_3$ and $AuBr_3$ which consist of dimeric planar molecules, are soluble



The main initial material for obtaining other compounds of gold is $AuCl_3$, which is got from the interaction of powdered Au and excess Cl_2 at 200 °C.

The halides, oxide, and hydroxide of Au(III) are amphoteric compounds with a predominance of acidic properties; $Au(OH)_3$, for instance, is easily dissolved in alkalis, with the formation of hydroxyaurates(III):

$$NaOH + Au(OH)_3 = Na[Au(OH)_4]$$

Even the dissolution of $Au(OH)_3$ in acids proceeds through the formation of anion complexes

$$Au(OH)_3 + 4HNO_3 = H[Au(NO_3)_4] + 3H_2O$$

Nitroaurates(III) and cyanaurates(III) of hydrogen have been isolated in the free state. In the presence of salts of the alkali metals, nitrate $\overset{+1}{M}[Au(NO_3)_4]$, sulphate $\overset{+1}{M}[Au(SO_4)_2]$, cyanate $\overset{+1}{M}[Au(CN)_4]$, sulphide $\overset{+1}{M}[AuS_2]$ and aurates(III) of other types are formed.

The acidic nature of Au(III) halides is seen in their extraordinary ability to yield $\overset{+1}{M}[AuHal_4]$ halogen aurates(III) (the stability constant of the $[AuCl_4]^-$ ion is 2×10^{21}). Most halogen aurates(III) are readily soluble in water and organic solvents.

The special tendency of Au(III) to form anion complexes is displayed during hydrolysis of its trihalides

$$AuCl_3 + H_2O \rightleftarrows H[Au(OH)Cl_3]$$
$$AuCl_3 + H_2O \rightleftarrows H_2[AuOCl_3]$$

The acid $H_2[AuOCl_3]$, which is formed during hydrolysis, reacts with Ag^+ ions to give a barely soluble salt $Ag_2[AuOCl_3]$ rather than AgCl, which indicates that the $[AuOCl_3]^{2-}$ ion is very stable.

Blue $K_3[CuF_6]$ and yellow $K[AgF_4]$ are known for Cu(III) and Ag(III). When $Cu(OH)_2$ is oxidised in an alkaline medium, hydroxy- and oxycuprates(III) of the type of $KCuO_2$ and $K[Cu(OH)_4]$ are formed:

$$\overset{+2}{Cu}(OH)_2 + NaClO + 2NaOH = 2Na\overset{+3}{Cu}O_2 + NaCl + 3H_2O$$

The +3 oxidation state of copper and silver is stabilized in complex iodates(VII) and tellurates(VI), e.g. $K_7[Cu(IO_6)_2] \cdot 7H_2O$, $Na_9[Cu(TeO_6)_2]$ (brown), and $K_6H[Ag(IO_6)_2] \cdot 10H_2O$, and $Na_6H_3[Ag(TeO_6)_2] \cdot 20H_2O$ (yellow). Compounds of Cu(III) and Ag(III) are strong oxidants.

All soluble compounds of copper, silver and gold are *poisons*!

CHAPTER 9

Group II *d* Elements

Zinc Zn, cadmium Cd, and mercury Hg are full electron analogues, and are the last *d* elements in their periods. Consequently the d^{10} configuration of the electron shell is fully stabilized with them. In this respect they differ from the other *d* elements, and resemble, on the contrary, the *p* elements of the long periods. Certain of their characteristics are as follows

	$_{30}$Zn	$_{48}$Cd	$_{80}$Hg
Atomic mass	65.37	112.40	200.59
Valence electrons	$3d^{10}4s^2$	$4d^{10}5s^2$	$5d^{10}6s^2$
Metallic atom radius, nm	0.139	0.156	0.160
Ion E^{2+} radius, nm	0.083	0.099	0.112
Ionisation energy, eV			
$E^0 \rightarrow E^+$	9.39	8.99	10.44
$E^+ \rightarrow E^{2+}$	17.96	16.9	18.8
$E^{2+} \rightarrow E^{3+}$	39.7	37.5	32.4
Abundance, mole per cent	1.5×10^{-3}	7.6×10^{-6}	7×10^{-7}

The first two ionisation energies of elements of the zinc subgroup are higher than those of *d* elements of the corresponding periods, which is due to penetration of the outer ns^2 electrons through the screen of $(n-1)d^{10}$ electrons. The diminishing ionisation energy in the transition from Zn to Cd is due to the high value of the principal quantum number *n*; the further increase of the ionisation energy of Hg is due to the penetration of the $6s^2$ electrons through the screen of the $4f^{14}$ electrons as well as through the screen of the $5d^{10}$ electrons. The third ionisation energies are quite high, which indicates that the $(n-1)d^{10}$ electron configuration is stable. The highest oxidation state of the elements in the zinc subgroup is accordingly +2. At the same time, the $(n-1)d^{10}$ electrons of zinc and its analogues (as of other *d* elements) are capable of a donor-acceptor interaction. As the size of the $(n-1)d$ orbitals increases in the Zn^{2+}—Cd^{2+}—Hg^{2+} series, the electron-donating power of the ions increases. There is a marked tendency to form complex compounds in the $E^{2+}(d^{10})$ ions.

The high stability of the $6s^2$ electron pair of mercury puts its stamp on all the element's properties, and conditions its essential difference from zinc and cadmium. In particular it is why most mercury compounds are unstable in contrast to those of zinc and cadmium. Again, in contrast to Zn and Cd, mercury has a series of derivatives of its cluster radical Hg_2^{2+} in which the atoms are linked together by a covalent —Hg—Hg— bond, i.e. a $6s^2$ configuration arises again. The oxidation state of mercury in Hg_2^{2+} derivatives is taken as +1.

9.1. The Zinc Subgroup

Zinc occurs in the Earth's crust as a mixture of six stable isotopes, cadmium of eight, and mercury of seven. Numerous artificial radioactive isotopes have been synthesised.

The most important minerals of Zn, Cd, and Hg are *zinc blende* (*sphalerite*) ZnS, *cinnabar* HgS, *smithsonite* $ZnCO_3$, and *greenockite* CdS. Zinc and its analogues also occur in polymetallic ores. Native mercury occurs in nature.

The simple substances. Zinc, cadmium, and mercury are silvery white metals, but in damp air they become coated with an oxide film and lose their lustre. All three metals (mercury in particular) are low-melting. Certain of their physical constants are as follows:

	Zn	Cd	Hg
Density, g/cm³	7.1	8.7	13.55
M.p., °C	419	321	39
B.p., °C	907	767	357
Electrical conductivity	16	13	1
$\Delta H^\circ_{subl.,\,298}$, kJ/mol	140	112	61
E°_{298}, $E^{2+} + 2e^- = E$, V	—0.76	—0.40	0.85
S°_{298}, J/K·mol	33	51	77

Their chemical activity is lower than that of the alkaline earth metals. In contrast to the calcium subgroup, their chemical activity (as in other subgroups of *d* elements except the scandium subgroup) weakens with increasing atomic weight. This is also indicated by the ΔG°_f of the dichlorides and the character of the changes in this value with atomic number (Fig. 247). The values of the metals' electrode potentials are further evidence of this. Zinc and cadmium come before hydrogen and mercury after it in the electromotive series.

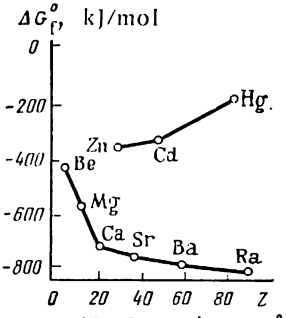


Fig. 247. Dependence of ΔG_f of dichlorides of Group II elements on atomic number

Zinc is a chemically active metal, readily soluble in acids and alkalis (with heating):

$$Zn + 2OH_3^+ + 2H_2O = H_2 + [Zn(OH_2)_4]^{2+}$$

$$Zn + 2H_2O + 2OH^- = H_2 + [Zn(OH)_4]^{2-}$$

Cadmium is practically insoluble in alkalis, and in acids dissolves less vigorously than zinc. Mercury is soluble only in acids that are quite strong oxidants because of their anions; derivatives of both Hg(II) and Hg(I) can be obtained. $Hg(NO_3)_2$, for example, is produced in the reaction between Hg and concentrated nitric acid:

$$Hg + 4HNO_3 = Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

When dilute HNO_3 acts on excess Hg, $Hg_2(NO_3)_2$ is obtained:

$$6Hg + 8HNO_3 = 3Hg_2(NO_3)_2 + 2NO + 4H_2O$$

Zinc and cadmium behave much more actively in relation to HNO_3 and concentrated H_2SO_4. Zinc, for example, reduces very dilute nitric acid to the ammonium ion:

$$4Zn + 10\overset{+5}{H}\overset{}{N}O_3 = 4Zn(NO_3)_2 + \overset{-3}{N}H_4NO_3 + 3H_2O$$

Zinc and its analogues react quite vigorously, when heated, with active nonmetals; interestingly, mercury reacts with sulphur and iodine even in normal conditions.

Zinc, cadmium, and mercury readily form alloys both with each other and with other metals. Mercury alloys, known as *amalgams*, are mostly fluid or paste-like. They can be obtained by triturating, or even by simply mixing the metal with mercury. When sodium is triturated with mercury, an exothermic process takes place and no less than seven intermetallic compounds are found in the amalgam. Amalgamated cadmium is a metallic solution. One of the methods for extracting gold from ores is based on its solubility in mercury.

Unlike the alkaline earth metals, zinc and cadmium can be obtained in the free state either by chemical reduction or by electrolysis of solutions of their compounds. The pyrometallurgical extraction of Zn and Cd from sulphide ores consists of two steps, the ores being first roasted and then the oxides obtained reduced by carbon:

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$

$$ZnO + C = Zn + CO$$

Because of the low stability of HgO ($\Delta G^\circ_{f,298} = -59$ kJ/mol), mercury is obtained from HgS in one step:

$$HgS + O_2 = Hg\,(l) + SO_2$$

With the hydrometallurgical method, zinc is extracted by leaching the roasted ore by dilute sulphuric acid, and electrolysing the $ZnSO_4$ solution obtained. Cadmium is usually displaced from sulphate solutions by metallic zinc.

Most of the zinc mined is used for galvanising iron (rust-protection) and in various alloys, the most important of which are *brass* (60 per cent Cu, 40 per cent Zn), *tombac* (90 per cent Cu, 10 per cent Zn), and *German silver* (65 per cent Cu, 20 per cent Zn, 15 per cent Ni). Cadmium is used in the control rods of atomic reactors, in low-melting alloys, in electroplating, as electrodes for alkali cells, in mechanically strong copper-cadmium alloys for electric conductors, etc. Mercury is widely used as a cathode in the electrochemical production of sodium hydroxide and chlorine, as a catalyst in organic synthesis (e.g. in the production of acetic acid), and for making rectifiers, mercury lamps, pressure gauges, etc.

9.2. Compounds of the Zinc Subgroup Elements

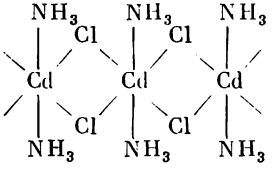
Compounds of zinc(II), cadmium(II), and mercury(II). The most characteristic coordination number of Zn(II) is four and of Cd(II) six. Coordination numbers of two, four, and six are about equally characteristic of mercury(II) (see Table 56).

Table 56. **Spatial Configuration of Complexes (Unit Cells) of the Zinc Subgroup Elements**

Coordination number	Spatial configuration of complexes	Typical compounds
4	Tetrahedron	$K_2[Zn(OH)_4]$, $[Zn(OH_2)_4]SO_4$, $[Zn(NH_3)_4]Cl_2$, $[Zn(NH_3)_2Cl_2]$, ZnO, ZnS, CdS, HgS, ZnCl
6	Octahedron	$[Cd(NH_3)_6](NO_3)_2$, CdO, $[Cd(NH_3)_2Cl_2]$, $CdBr_2$, $CdCl_2$
2	Linear	$HgNH_2Cl$, HgO, $Hg(CN)_2$

A coordination number of four is displayed in E(II), e.g. in crystals of ZnO, ZnS, CdS, ESe, ETe, HgS (tetrahedrotetrahedral coordination of atoms), $Zn(OH)_2$ (tetrahedroangular). The structures of the two forms of zinc sulphide, cubic sphalerite (α-ZnS) and hexagonal wurtzite (β-ZnS), with tetrahedral bonds are illustrated in Fig. 194.

A coordination number of six is observed in crystals of CdO (NaCl type lattice). Crystals of $CdBr_2$, CdI_2, $Cd(OH)_2$, Cd(OH)Cl, and Zn(OH)Cl have a layer structure (see Fig. 234) formed by octahedral CdX_6 units, which also form $CdCl_2 \cdot 2H_3N$ in which the chlorine atoms act as bridge bonds between the Cd atoms while the NH_3 molecules occupy the free coordination points:



In contrast to the elements of the calcium subgroup, the stability of similar binary compounds of the elements of the zinc subgroup decreases with the increasing atomic number as can be judged from the character of the changes in the values of ΔG_f° (kJ/mol):

ZnO	CdO	HgO
—321	—229	—59
ZnS	**CdS**	**HgS**
—200	—153	—51

The decrease in the stability of compounds is especially marked in the transition from Cd to Hg, e.g. $Zn(OH)_2$ and $Cd(OH)_2$ are stable,

while no hydroxide of Hg(II) is known, since it decomposes into HgO and water the moment it is formed:

$$Hg(NO_3)_2\ (sol) + 2KOH\ (sol) = HgO\ (s) + 2KNO_3\ (sol) + H_2O\ (l)$$

No carbonate of Hg(II) is known. The decomposition temperatures of ZnO and CdO are 1950 °C and 1813 °C respectively, but HgO decomposes into the simple substances at 400 °C. Hg_3N_2 and HgC_2 are also unstable and decompose explosively.

Coloured compounds to be noted are brown CdO, red HgI_2, and yellow CdS; HgS can exist in two forms, black and red. The black HgS obtained in exchange reactions turns into the red form on sublimation. Cinnabar is also red. Depending on its degree of dispersion, HgO may be either red or yellow.

The halides (except ZnF_2, $HgBr_2$, and HgI_2), sulphates, nitrates, and certain compounds of zinc and its analogues are water soluble. Many of them are soluble in organic solvents.

When E(II) compounds are dissolved in water, and when EO or $E(OH)_2$ react with acids, stable $[E(OH_2)_4]^{2+}$ and $[E(OH_2)_6]^{2+}$ aquo complexes are formed. Crystal hydrates are therefore very characteristic of Zn(II), Cd(II), and Hg(II), e.g. $Zn(NO_3)_2 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$, $Zn(BrO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot 2H_2O$, and $Hg(ClO_4)_2 \cdot 6H_2O$. The most stable of the other cation complexes are the $[E(NH_3)_4]^{2+}$ and $[E(NH_3)_6]^{2+}$ ammino complexes easily formed by the action of ammonia on salt solutions:

$$ZnSO_4 + 4H_3N = [Zn(NH_3)_4]SO_4$$

The formation of ammoniates explains the ready solubility of $E(OH)_2$ in the presence of ammonia:

$$Cd(OH)_2 + 6H_3N = [Cd(NH_3)_6](OH)_2$$

Ammoniates of mercury(II), e.g. $[Hg(NH_3)_4](NO_3)_2$, are formed only with a great excess of H_3N and in the presence of ammonia salts. The interaction of $HgCl_2$ and H_3N in a concentrated solution of NH_4Cl leads to the formation of a precipitate $[Hg(NH_3)_2Cl_2]$:

$$HgCl_2 + 2H_3N = [Hg(NH_3)_2Cl_2]$$

In dilute solutions an amide derivative $HgNH_2Cl$, insoluble in water, is produced:

$$HgCl_2 + 2H_3N = HgNH_2Cl + NH_4Cl$$

Zinc and its analogues form various *zincates*, *cadmates*, and *mercurates*: $Zn(OH)_2$, for instance, dissolves easily in alkalis with formation of soluble hydroxyzincates:

$$Zn(OH)_2 + 2KOH = K_2[Zn(OH)_4]$$

The amphoteric character of $Zn(OH)_2$ and its behaviour in acids and alkalis can be expressed as follows:

$$[Zn(OH_2)_4]^{2+} \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} Zn(OH)_2 \underset{OH_3^+}{\overset{OH^-}{\rightleftharpoons}} [Zn(OH)_4]^{2-}$$

Zinc amide (dihydronitride) $Zn(NH_2)_2$ behaves in the same way in liquid ammonia. And just as $Zn(OH)_2$ is insoluble in water, so $Zn(NH_2)_2$ is insoluble in liquid ammonia, but is readily soluble in the presence of ammono acids and ammono bases

$$[Zn(NH_3)_4]^{2+} \underset{NH_4^+}{\overset{NH_2^-}{\rightleftharpoons}} Zn(NH_2)_2 \underset{NH_4^+}{\overset{NH_2^-}{\rightleftharpoons}} [Zn(NH_2)_4]^{2-}$$

Ammoniates are formed in the presence of excess NH_4^+ ions and dihydronitride zincates (amidozincates) in the presence of excess NH_2^- ions.

Cadmium hydroxide does not display acidic properties as much as $Zn(OH)_2$ but when boiled for a long time in a concentrated alkali, it forms hydroxycadmates, e.g. $K_4[Cd(OH)_6]$ and $Ba_2[Cd(OH)_6]$; these, however, are easily decomposed by water in the absence of excess alkali. More or less stable hydroxymercurates have not been obtained.

Complexes with CN^- π acceptor ligands of the type of $[E(CN)_4]^{2-}$, which are easily formed by the action of basic cyanide on solutions of E(II) salts, are most stable. The $E(CN)_2$ being formed first precipitates, but dissolves in an excess of the basic cyanide:

$$2KCN + E(CN)_2 = K_2[E(CN)_4]$$

Because of an increasing capacity for a π dative interaction in the Zn^{2+}—Cd^{2+}—Hg^{2+} series, the stability of complexes with the ligands capable of accepting electron pairs increases, e.g.

	$[ZnCl_4]^{2-}$	$[CdCl_4]^{2-}$	$[HgCl_4]^{2-}$
$\log K_{st}$	—1.52	1.7	15.22
	$[ZnI_4]^{2-}$	$[CdI_4]^{2-}$	$[HgI_4]^{2-}$
$\log K_{st}$	—0.5	5.35	29.83

The stability of mercury(II) halide complexes increases in the F^-—Cl^-—Br^-—I^- series for the same reason, e.g.

	$[HgCl_4]^{2-}$	$[HgBr_4]^{2-}$	$[HgI_4]^{2-}$
$\log K_{st}$	15.22	21.00	29.83

Thus, while the complex halides of Zn(II) can be regarded as double salts as regards stability, those of Hg(II) are very stable and easily formed in solutions; HgI_2, for instance, which is insoluble in water

readily dissolves in excess basic iodide:

$$2KI + Hg(NO_3)_2 = HgI_2 + 2KNO_3$$
$$2KI + HgI_2 = K_2[HgI_4]$$

The ability of HgS to dissolve in solutions of basic sulphides can be explained in the same way:

$$K_2S + HgS = K_2[HgS_2]$$

Numerous derivatives of anion complexes of the type of $\overset{+1}{M}_2[E(SCN)_4]$, $\overset{+1}{M}_2[E(SO_3)_2]$, and $\overset{+1}{M}_2[E(NO_3)_4]$, which can be regarded as double salts as regards stability, and their crystal hydrates, e.g. $\overset{+1}{M}_2[E(SO_4)_2]\cdot 6H_2O$, are known.

Derivatives of mercury(II) have oxidising properties

$$2Hg^{2+} + 2e^- = Hg_2^{2+}, \qquad E^\bullet_{298} = 0.92 \text{ V}$$
$$Hg^{2+} + 2e^- = Hg, \qquad E^\bullet_{298} = 0.85 \text{ V}$$

for example

$$Hg(NO_3)_2 + Hg \rightleftarrows Hg_2(NO_3)_2$$
$$HgCl_2 + SO_2 + 2H_2O = Hg + H_2SO_4 + 2HCl$$

Compounds of mercury(I). A black oxide Hg_2O, Hg_2Hal_2 halides and certain salts are known for Hg(I). Most mercury(I) compounds are colourless and barely soluble in water; $Hg_2(NO_3)_2\cdot 2H_2O$, the main initial material for obtaining other Hg(I) derivatives, is readily soluble. X-ray crystallography reveals the presence of an $[H_2O—Hg—Hg—OH_2]^{2+}$ ion in the crystal of $Hg_2(NO_3)_2\cdot 2H_2O$.

Depending on the conditions, the compounds of Hg_2^{2+} may have either reducing or oxidising properties, e.g.

$$Hg_2Cl_2 + Cl_2 = 2HgCl_2$$
$$Hg_2Cl_2 + SnCl_2 = 2Hg + SnCl_4$$

They readily undergo disproportionation, with the liberation of free mercury and formation of corresponding mercury(II) compounds:

$$Hg_2^{2+} = Hg\ (l) + Hg^{2+}, \qquad E^\bullet_{298} = -0.131 \text{ V}$$

In some cases decomposition is so rapid that the Hg_2^{2+} derivatives cannot be isolated; Hg_2S and $Hg_2(CN)_2$, for example, cannot be formed by exchange reactions since they break down immediately into free mercury, insoluble HgS, and low-dissociating $Hg(CN)_2$. Hg_2Cl_2 and Hg_2SO_4 are more stable but they too are decomposed by slight heating and intense illumination.

Mercury compounds (the simple substance included) are extremely poisonous!

The applications of compounds of zinc and its analogues are quite varied. The sulphides, for instance, are used in the making of mineral paints. $HgCl_2$ (*corrosive sublimate*), Hg_2Cl_2 (*calomel*), and other preparations of mercury and zinc are used in medicine. Crystalline ZnS, prepared in a special way, fluoresces in the dark after preliminary illumination; this property is employed in work with radioactive preparations and in X-ray engineering. Cadmium sulphide CdS is used as a photosensitive resistor whose resistance depends on the intensity of illumination. A concentrated solution of $ZnCl_2$, which dissolves cellular tissues, is used in the manufacture of parchment paper.

IV

THE CHEMISTRY OF *f* ELEMENTS

CHAPTER 1

Sixth Period *f* Elements

The *f* elements (like *d* elements) are transition elements. They are located in the 6th (*4f* elements) and 7th (*5f* elements) periods of the periodic system. The *4f* elements make up the family of *lanthanides* and *5f* elements the family of *actinides*. The *f* elements are usually placed in group III, in the scandium subgroup.

1.1. The Lanthanides

The lanthanide family comprises cerium Ce, praseodymium Pr, neodymium Nd, promethium Pm, samarium Sm, europium Eu, gadolinium Gd, terbium Tb, dysprosium Dy, holmium Ho, erbium Er, thulium Tm, ytterbium Yb, and lutetium Lu.

As will be seen from Table 57, the electron configuration of the atoms of the lanthanides can be expressed by the formula $4f^{2-14}5s^25p^65d^{0-1}6s^2$. The third outer shell (*4f* subshell) is being filled with electrons, while the number of electrons in the outermost shell ($6s^2$) and in the penultimate ($5s^25p^6$) shell of most lanthanides is identical. The chemical and spectroscopic data indicate that although the *4f* and *5d* states are very similar as regards energy in the lanthanides, the *4f* state proves to be even more advantageous. Therefore a *5d* electron is transferred to the *4f* state in their atoms in contrast to La (except in Gd).

The elements of the lanthanide family are subdivided into *subfamilies* according to the filling of the *4f* orbitals. The first seven elements (Ce—Gd), in which (in accordance with the Hund rule) the *4f* orbitals are filled by one electron, are classed as the *cerium subfamily*, while the other seven elements (Tb—Lu), in which the *4f* orbitals are filled by a second electron, are grouped together in the *terbium subfamily*:

							La $4f^05d^1$
Cerium subfamily	**Ce** $4f^2$	**Pr** $4f^3$	**Nd** $4f^4$	**Pm** $4f^5$	**Sm** $4f^6$	**Eu** $4f^7$	**Gd** $4f^75d^1$
Terbium subfamily	**Tb** $4f^{7+2}$	**Dy** $4f^{7+3}$	**Ho** $4f^{7+4}$	**Er** $4f^{7+5}$	**Tm** $4f^{7+6}$	**Yb** $4f^{7+7}$	**Lu** $4f^{14}5d^1$

Table 57. **Selected Constants of Lanthanides**

	Element	Symbol	Atomic No.	Electron structure					Metallic radius of atom, nm	Ion E^{3+} radius, nm	Ionisation energy $E^0 - E^{3+}$, eV	Oxidation state
				4f	*5s*	*5p*	*5d*	*6s*				
	Barium	Ba	56	—	2	6	—	2	0.221	—	5.21	+2
	Lanthanum	La	57	—	2	6	1	2	0.187	0.104	5.58	+3
Cerium subfamily	Cerium	Ce	58	2	2	6	—	2	0.183	0.102	5.5	+3, +4
	Praseodymium	Pr	59	3	2	6	—	2	0.182	0.100	5.42	+3, +4
	Neodymium	Nd	60	4	2	6	—	2	0.182	0.099	5.49	+3
	Promethium	Pm	61	5	2	6	—	2	0.180	0.098	5.55	+3
	Samarium	Sm	62	6	2	6	—	2	0.181	0.097	5.63	+3, +2
	Europium	Eu	63	7	2	6	—	2	0.202	0.094	5.66	+3, +2
	Gadolinium	Gd	64	7	2	6	1	2	0.179	0.094	6.16	+3
Terbium subfamily	Terbium	Tb	65	9	2	6	—	2	0.177	0.089	5.85	+3, +4
	Dysprosium	Dy	66	10	2	6	—	2	0.177	0.088	5.93	+3, (+4)
	Holmium	Ho	67	11	2	6	—	2	0.176	0.086	6.02	+3
	Erbium	Er	68	12	2	6	—	2	0.175	0.085	6.10	+3
	Thulium	Tm	69	13	2	6	—	2	0.174	0.085	6.18	+3, (+2)
	Ytterbium	Yb	70	14	2	6	—	2	0.193	0.081	6.25	+3, +2
	Lutetium	Lu	71	14	2	6	1	2	0.174	0.050	5.43	+3
	Hafnium	Hf	72	14	2	6	2	2	0.159	—	7.5	+4

In Gd and Lu, as in La, the extra electron over and above the stable f^7 and f^{14} configuration is at the 5*d* state.

When very slightly excited, one of the 4*f* electrons (less often two) is transferred to the 5*d* state, while the others (screened from external influences by the $5s^25p^6$ electrons) have no significant effect on the chemical properties of most lanthanides. Their properties are thus mainly determined by the $5d^16s^2$ electrons so that they have a great similarity to group III *d* elements, i.e. scandium and its analogues. The greatest similarity to the lanthanides is found in yttrium and lanthanum, whose atomic and ionic radii are close to those of the elements in the family.

Since the difference in structure of the atoms is exclusively in the third outer layer, which does not greatly affect their chemical prop

erties. all the lanthanides are extremely alike and because of this special similarity of properties are often classed together with lanthanum, yttrium, and with scandium, in a single family, that of the *rare earth elements.**

Although so extremely similar, the lanthanides have their differences. Some of their properties change uniformly in the transition from one element to the other in the Ce—Lu series, while others alter periodically. The uniformity is due to the *lanthanide contraction*, i.e. the gradual decrease in atomic and ionic radii in the Ce—Lu series.

The periodic character of the filling of the $4f$ orbitals (first with one electron and then with two) determines the *inner periodicity* of the variation of certain properties of the lanthanides and their compounds.

Since the $5d^16s^2$ electrons are mainly valence electrons in the lanthanides, their stable oxidation state is $+3$. The elements adjacent to lanthanum ($4f^0$), gadolinium ($4f^7$) and lutetium ($4f^{14}$), however, have variable oxidation states; thus, apart from a $+3$ oxidation state, cerium ($4f^26s^2$) has one of $+4$, which is connected with the transition of two $4f$ electrons to the $5d$ state. For the same reason praseodymium ($4f^36s^2$) may also display a $+4$ oxidation state, although this is much less characteristic of it than of Ce. On the other hand, europium, which has seven $4f$ electrons ($4f^76s^2$), can have an oxidation state of $+2$.

A similar relationship occurs with the elements in the terbium subfamily although, owing to pairing of the $4f$ electrons, it is less pronounced; terbium ($4f^96s^2$) and dysprosium ($4f^{10}6s^2$) may exhibit a $+4$ oxidation state and ytterbium ($4f^{14}6s^2$) and thulium ($4f^{13}6s^2$) $+2$.

The periodic character of the variation in oxidation state can be clearly seen from the following table:

						La
						+3
Ce	Pr	Nd	Pm	Sm	Eu	Gd
+3, +4	+3, +4, (+5?)	+3	+3	+3, +2	+3, +2	+3
Tb	Dy	Ho	Er	Tm	Yb	Lu
+3, +4	+3, (+4)	+3	+3	+3, (+2)	+3, +2	+3

The differences in properties of the cerium elements linked with the lanthanide contraction and the character of the filling of $4f$ orbitals are not, of course, great, but when seen against the background

* The rare earth elements, in turn, are divided into the *cerium* (La, Ce, Pr, Nd, Pm, Sm, Eu) and *yttrium* (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) elements.

of the extraordinary similarity of these elements they are very important, especially for separating the lanthanides from one another.

The abundance of the lanthanides is comparable to that of iodine, antimony, and copper, but they are very dispersed. More than 250 minerals containing lanthanides are known. Those with even atomic numbers are more abundant than those with odd ones (see Fig. 123).

Lanthanides with odd atomic numbers have only one natural isotope (except europium and lutetium, which have two). The even-number lanthanides have several isotopes (except erbium and cerium which have six and four natural isotopes respectively). Artificial, radioactive isotopes have been obtained for all the rare earth elements, in particular from nuclear reactors.

The elements of the family always occur together in nature, and also with lanthanum and yttrium. The most important minerals for recovering rare earth elements are *monazite* EPO_4, *bastnaesite* $EFCO_3$, and *loparite* $(Na, Ca, E)_2 (Ti, Nb, Ta)_2O_6$.

Promethium is a radioactive element and is seldom found in the Earth's crust. It was first discovered in 1947 in the uranium fission products in atomic reactors; it is obtained artificially.

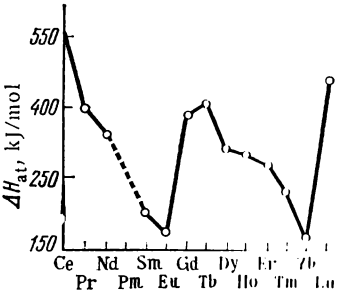


Fig. 248. Dependence of the enthalpy of atomisation of lanthanides on atomic number

The simple substances. As simple substances, the elements of the lanthanides are high-melting, silvery white metals (Pr and Nd are slightly yellowish). Certain of their constants are given in the table below (with those of lanthanum for comparison):

	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd
Density, g/cm³	6.12	6.77	6.77	7.01	—	7.54	5.24	7.89
M.p., °C	920	798	931	1018	1042	1072	822	1311
B.p., °C	3370	3470	3017	3210	—	1670	1430	2830
		Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Density, g/cm³	—	8.25	8.56	8.78	9.06	9.32	6.95	9.85
M.p., °C	—	1360	1409	1470	1522	1545	824	1656
B.p., °C	—	2480	2330	2380	2390	1720	1320	2680

As will be seen from the table, there is an inner regularity in the transition from Ce to Lu in the variation of density and melting and boiling points. These constants are minimum with Eu and Yb, which will also be seen from Fig. 248, which shows the dependence of the lanthanides' enthalpy of atomisation (sublimation) on atomic number. The low enthalpies of europium and ytterbium are probably due

to the involvement of two 6*s* electrons only in the formation of bonds in these elements because of the stability of the nonbonding configuration $4f^7$ and $4f^{14}$.

The lanthanides are malleable and relatively soft; their electrical conductivity is similar to that of mercury.

Like La, the lanthanides come after the alkali and alkaline earth metals in chemical activity. The compact metals are quite stable in dry air, but rapidly become dull when it is humid. When heated to between 200 °C and 400 °C, they ignite in air and burn to form mixtures of oxides and nitrides. Powdered cerium is even pyrophoric, i.e. ignites spontaneously in air in normal conditions. The pyrophoric properties of cerium and other lanthanides are utilised in the making of pyrophoric alloys, the flints of cigarette lighters, tracer bullets, etc.

Lanthanides react with the halogens and (when heated) with nitrogen, sulphur, carbon, silicon, phosphorus, hydrogen, etc. They alloy with most metals and often form intermetallic compounds. Their activity can be judged from the following values of their electrode potentials:

$$E^{3+} + 3e^- = E$$

Metal	Ce	Pr	Nd	Pm	Sm	Eu	Gd
E°_{298}, V	—2.48	—2.46	—2.43	—2.42	—2.41	—2.40	—2.40
Metal	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
E°_{298}, V	—2.39	—2.35	—2.32	—2.30	—2.28	—2.27	—2.25

Because they are far above hydrogen in the electromotive series, the lanthanides are oxidised by water (in particular by hot water) with liberation of hydrogen and react even more vigorously with acids. They are stable in HF and H_3PO_4, since they become covered with defensive films of insoluble salts. They do not dissolve in alkalis.

Because of the great similarity of their properties, the lanthanides are very difficult to separate from one another. At the present time this is done in ion-exchangers and by extraction of their compounds with organic solvents.

The lanthanides are usually obtained in the metallic state through reduction by calcium chloride or fluoride.

The rare earth metals have become of great importance of late. Their extraordinary capacity to combine with many gases is used in vacuum technology. In steel-making they are used as alloying admixtures to improve the mechanical properties of alloys. The lanthanides and their compounds are employed as catalysts in organic and inorganic synthesis, and also as materials in radio, electrical, and atomic power engineering.

1.2. Compounds of the Lanthanides

Lanthanide(III) compounds. Numerous binary compounds (E_2O_3, $EHal_3$, E_2S_3, EN, EH_3) and various salts are known for the lanthanides in the +3 oxidation state. The enthalpies and Gibbs' energies of formation of their similar compounds are similar as well, for example the ΔG_f° of their crystalline trichlorides are as follows (in kJ/mol):

$CeCl_3$	$PrCl_3$	$NdCl_3$	$PmCl_3$	$SmCl_3$	$EuCl_3$	$GdCl_3$	$TbCl_3$
—983	—1020	—963	—882	—863	—803	—928	—803

The variation of the enthalpy of atomisation of the trihalides with atomic number of the lanthanides is shown in Fig. 249. Low enthal-

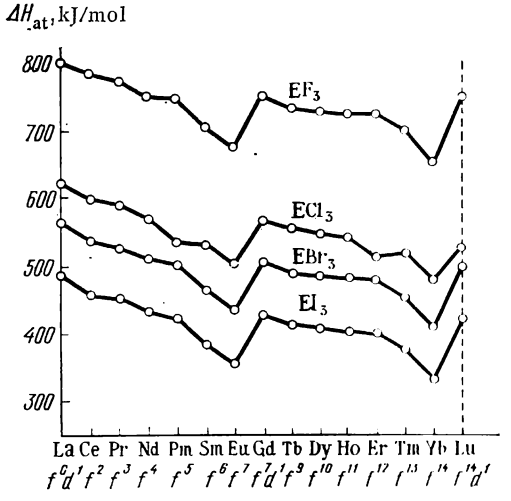


Fig. 249. Dependence of the enthalpy of atomisation of lanthanide trihalides on atomic number of the elements

pies of atomisation of the trihalides of europium ($4f^76s^2$) and ytterbium ($4f^{14}6s^2$) indicate the increasing stability of the $4f^{14}$ electron configuration (complete filling of the $4f$ level) and $4f^7$ configuration (maximum number of unpaired $4f$ electrons). This can be explained by quantum-mechanical theory. The quite high bond energy is due to the $6s$ and $5d$ electrons, while the involvement of deeper $4f$ electrons in the formation of bonds reduces the enthalpy of atomisation, which becomes especially clear with the stablest f^7 and f^{14} configurations.

In contrast to d elements, the coordination number of f elements can exceed nine and be as high as ten, or even fourteen, which may

be due to the involvement of *f* orbitals in the formation of bonds. Certain polyhedral unit cells of the lanthanides(III) are illustrated in Fig. 250. High coordination numbers are more characteristic of the atoms of *f* elements located at the beginning of the family, while an octahedral structure is more characteristic of those completing the family.

The colour of E^{3+} ions changes regularly in accordance with the greater or lower stabilisation of the $4f$ state; for example, ions with

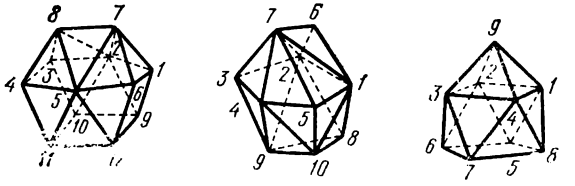


Fig. 250. Selected polyhedra corresponding to the characteristic coordination numbers of lanthanides (III)

$4f^0$, $4f^7$ and $4f^{14}$, and also with a $4f^1$ and $4f^{13}$ configuration are without colour, while the rest are more or less intensely coloured:

La^{3+} ($4f^0$)	colourless	Lu^{3+} ($4f^{14}$)
Ce^{3+} ($4f^1$)	colourless	Yb^{3+} ($4f^{13}$)
Pr^{3+} ($4f^2$)	green	Tm^{3+} ($4f^{12}$)
Nd^{3+} ($4f^3$)	reddish	Er^{3+} ($4f^{11}$)
Pm^{3+} ($4f^4$)	pink, yellow	Ho^{3+} ($4f^{10}$)
Sm^{3+} ($4f^5$)	yellow	Dy^{3+} ($4f^9$)
Eu^{3+} ($4f^6$)	pale pink	Tb^{3+} ($4f^8$)
Gd^{3+} ($4f^7$)	colourless	Gd^{3+} ($4f^7$)

The colour of the E^{3+} ions is due to the *f-f* transition. Since the $4f$ electrons are effectively screened from external effects by the $5s^2$ and $5p^6$ subshells, the colour of the ions does not depend on the nature of their coordinational structure.

The *oxides* of lanthanides E_2O_3 have high enthalpies and Gibbs' energies of formation (ΔG_f° of the order of -1600 kJ/mol) and refractoriness (melting points of the order of 2000 °C). The oxides are basic compounds, practically insoluble in water, but reacting with it to form hydroxides and liberate heat. The E_2O_3 oxides are readily soluble in HCl and HNO_3, but (like Al_2O_3) lose their chemical activity after calcining. They do not react with alkali solutions. Crystalline compounds with a $LiEO_2$ or $NaEO_2$ composition, however, have been obtained, which indicates the amphoteric character of E_2O_3. Their colour depends on the electron configuration of the E^{3+} ion (see above).

The *hydroxides* $E(OH)_3$ are obtained through exchange reactions. With the decreasing radii in the series Ce^{3+}—Lu^{3+}, the basic character

of the hydroxides weakens slightly, their amphoteric character strengthens, their thermal stability falls, and their solubility diminishes. Thus, the solubility product of $La(OH)_3$ is 1.0×10^{-19}, of $Ce(OH)_3$ and $Pr(OH)_3$ 10^{-20}, falling further to 2.5×10^{-24} in $Lu(OH)_3$.

Lanthanide(III) salts soluble in water are the chlorides ECl_3, nitrates $E(NO_3)_3$, and sulphates $E_2(SO_4)_3$; the fluorides EF_3, carbonates $E_2(CO_3)_3$, and phosphates EPO_4 are difficult to dissolve.

The crystal hydrates of the lanthanides(III) have a variable number of water molecules, e.g. $E(NO_3)_3 \cdot 6H_2O$, $EBr_3 \cdot 6H_2O$, $E_2(SO_4)_3 \cdot 8H_2O$, $Nd(BrO_3)_3 \cdot 9H_2O$. The colour of aquo complexes depends on the electron configuration of the E^{3+} ion.

Double salts, for example $3Mg(NO_3)_2 \cdot 2E(NO_3)_3 \cdot 24H_2O$, $M^{+1}_2E(NO_3)_5 \cdot 4H_2O$, $3Na_2SO_4 \cdot E_2(SO_4)_3 \cdot 12H_2O$ are quite typical of the lanthanides(III). The $[Ce(NO_3)_6]^{3-}$ ion has the configuration of a dodecahedron (by the O atoms), the $[Ce(NO_3)_5]^{2-}$ ion of a decahedron, and the $[Nd(OH_2)_9]^{3+}$ ion of a nonahedron. There are very many complexes of the lanthanides with a chelate type of ligands.

Various complexes with organic ligands (which are very important for separation of the rare earth metals) are known.

The *hydrides* of lanthanides are formed by interaction of the simple substances (at 300 °C to 400 °C), the process being quite active. All lanthanides form hydrides of an EH_2 composition, and also (except europium and ytterbium) compounds with a composition approaching EH_3. The specific behaviour of Eu and Yb is probably due to the stability of the $4f^7$ and $4f^{14}$ configurations.

The EH_2 hydrides have a structure of the fluorite type (see Fig. 70*a*). They are salt-like compounds more or less resembling the ionic hydrides of the alkaline earth metals, but with little in common with the hydrides of *d* elements. The hydrogen compounds of the lanthanides are quite active chemically, reacting vigorously with water, oxygen, the halogens, and other oxidants. The EH_3 compounds are especially reactive.

The oxides, sulphides, nitrides and carbides of the lanthanides are high-melting compounds and are therefore used for making refractory ceramics. Lanthanide compounds are also used to produce special grades of glass.

Lanthanide(IV) compounds. As already pointed out, a +4 oxidation state is characteristic of cerium and can also be found with terbium and praseodymium. For cerium(IV) a pale yellow oxide CeO_2, white fluoride CeF_4, yellow hydroxide $CeO_2 \cdot nH_2$, and a few salts, e.g. $Ce(ClO_4)_4$ and $Ce(SO_4)_2$, have been obtained. The dioxide CeO_2 formed by direct interaction of the simple substances or by thermal decomposition of certain cerium(III) salts. The dioxide is high-melting (m.p. 2500 °C) and quite inactive after calcining (not reacting with acids or alkalis).

The hydroxide $Ce(OH)_4$ is obtained from an exchange reaction in an aqueous solution in the form of a jelly-like precipitate of a variable $CeO_2 \cdot nH_2O$ composition. In contrast to $Ce(OH)_3$ it has amphoteric properties and dissolves in acids to form orange solutions, the colour being due to the formation of $[Ce(OH_2)_n]^{4+}$ aquo complexes. The chemistry of Ce(IV) aqueous solutions is similar to that of Zr(IV) and Hf(IV). With few exceptions, the salts of cerium(IV) are unstable and strongly hydrolysed in water. The double salt of cerium(IV) are more stable, and orange crystals of $(NH_4)_2[Ce(NO_3)_6] \times \times 2H_2O$ are precipitated from HNO_3 solutions. The $[Ce(NO_3)_6]^{2-}$ ion has the configuration of an icosahedron (Ce^{4+} being surrounded with twelve oxygen atoms), i.e. the NO_3^- ion acts as a didentate ligand.

When $CeO_2 \cdot nH_2O$ are fused with an alkali, or CeF_4 with KF, oxycerates(IV) and fluocerates(IV) respectively are formed:

$$2NaOH + CeO_2 = Na_2CeO_3 + H_2O$$

$$2KF + CeF_4 = K_2CeF_6$$

In acid solutions, compounds of cerium(IV) act as quite strong oxidants ($E^\circ_{Ce^{4+}/Ce^{3+}} = 1.61$ V) and oxidise concentrated hydrochloric acid, for example:

$$2Ce(OH)_4 + 8HCl = 2CeCl_3 + Cl_2 + 8H_2O$$

The compounds of praseodymium(IV) and terbium(IV) are unstable and are strong oxidising agents.

Lanthanide(II) compounds. The + 2 oxidation state is more pronounced in europium. Derivatives of Eu(II), Sm(II), Yb(II) resemble compounds of elements of the calcium subgroup. The oxides EO and hydroxides $E(OH)_2$ are basic compounds. The sulphates ESO_4 (like $BaSO_4$) are insoluble in water.

Europium often occurs in minerals together with the elements of the calcium subgroup, while minerals containing the rare earth metals in the +3 oxidation state are, as a rule, poor in europium, which is further evidence that its +2 oxidation state is quite stable.

Lanthanides(II) derivatives are reducing agents.

CHAPTER 2

Seventh Period *f* Elements

The actinide family comprises thorium Th, protactinium Pa, uranium U, neptunium Np, plutonium Pu, americium Am, curium Cm, berkelium Bk, californium Cf, einsteinium Es, fermium Fm, mendelevium Md, nobelium No, and lawrencium Lr. Table 58 gives the main characteristics of their atoms and ions (for comparison's sake data are also given on radium, actinium, and kurchatovium).

Uranium U, thorium Th, and protactinium Pa occur in the Earth's crust. The other actinides do not occur in nature (except for insignificant quantities of neptunium and plutonium) and were obtained artificially from nuclear reactions between 1940 and 1961 (see p. 659). All actinides are radioactive, and the role of spontaneous fission of their nuclei becomes more pronounced with increasing nuclear mass. The half-life of uranium is about 10^{16} years with spontaneous fission; for plutonium it is 10^{10} years, for curium 10^{6} years, for californium

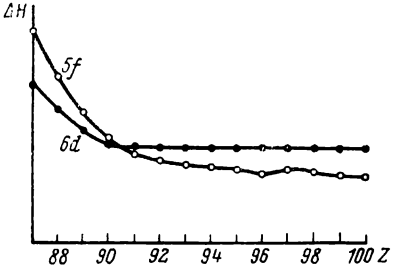


Fig. 251. Bond energy of 5*f* and 6*d* electrons with the nuclei of the heaviest elements

of the order of one year, and for fermium several hours. The half life of the most stable isotope of nobelium ^{256}No is 1500 seconds. At present $_{93}$Np and $_{94}$Pu can be obtained by the kilogram, $_{95}$Am and $_{96}$Cm by tens of grammes, $_{97}$Bk and $_{98}$Cf by milligrammes, $_{99}$Es by microgrammes, and the other actinides obtained only 'by the piece'. For that reason, only the first seven have been studied; the data available on the other elements of the family have been mainly obtained by studying the behaviour of their ions in solution, and by certain indirect studies. Chemical study of actinides is greatly complicated by their radioactive decay and radiation, which cause chemical changes in the systems being examined.

The spectroscopic, chemical, and other data indicate that the 7*s*, 6*d*, and 5*f* states of the atoms of the heaviest elements of the periodic system are very similar in energy. Determination of their electron configurations is therefore difficult. For protactinium, whose ground state can be expressed by the formula [Rn] $5f^2 6d^1 7s^2$, this state is so close to the $6d^3 7s^2$, $5f^1 6d^2 7s^2$, or $5f^3 7s^2$ state that it is difficult to determine with certainty which of them best describes the configuration of its atom in the ground state. As Fig. 251 shows the energy of the 5*f* electrons' bond with the nucleus gradually increases with increasing atomic number of the element, while that of the 6*d* electrons decreases. The transition of the 6*d* electrons to the 5*f* state therefore becomes more advantageous.

Table 58. Selected Data on the Actinides

Element	Symbol	Atomic No.	Electron structure	Metallic radius of atom, nm	Ion E^{3+} radius, nm	Ionisation energy $E \rightarrow E^{3+}$, eV	Oxidation state
Radium	Ra	88	$7s^2$	0.235	—	5.28	+2
Actinium	Ac	89	$6d^17s^2$	0.203	0.111	5.1	+3
Thorium	Th	90	$6d^27s^2$	0.180	0.108	6.1	(+3), +4
Protactinium	Pa	91	$5f^26d^17s^2$ or $5f^16d^27s^2$	0.162	0.106	5.9	(+3), +4, +5
Uranium	U	92	$5f^36d^17s^2$	0.153	0.104	6.2	+3, +4, +5, +6
Neptunium	Np	93	$5f^57s^2$	0.150	0.102	6.2	+3, +4, +5, +6, +7
Plutonium	Pu	94	$5f^67s^2$	0.162	0.101	6.06	+3, +4, +5, +6, +7
Americium	Am	95	$5f^77s^2$	—	0.100	5.99	+3, +4, +5, +6, +7
Curium	Cm	96	$5f^76d^17s^2$	—	0.098	6.09	+3, (+4)
Berkelium	Bk	97	$5f^86d^17s^2$ or $5f^97s^2$	—	—	6.30	+3, +4
Californium	Cf	98	$5f^{10}7s^2$	—	—	6.4	+2, +3, (+4)
Einsteinium	Es	99	$5f^{11}7s^2$	—	—	6.5	+2, +3
Fermium	Fm	100	$5f^{12}7s^2$	—	—	6.6	+2, +3
Mendelevium	Md	101	$5f^{13}7s^2$	—	—	6.7	+2, +3
Nobelium	No	102	$5f^{14}7s^2$	—	—	—	+2, +3
Lawrencium	Lr	103	$5f^{14}6d^17s^2$	—	—	—	+3
Kurchatovium	Ku	104	$6d^27s^2$	—	—	—	+4

Because of the special closeness of the 6*d* and 5*f* states, the elements of the thorium subfamily (Th—Cm) act as both *f* and *d* elements (indistinct periodicity). The actinides display variable oxidation states (see Table 58). As the 5*f* orbitals are filled with electrons, the configuration of the atoms is stabilised and it becomes more difficult for 6*d* electrons to pass to the 5*f* state. Elements of the berkelium subfamily (Bk—Lr) therefore behave like typical *f*-elements and their properties are similar to those of the lanthanides.

By analogy with the lanthanides, the first seven elements of the actinides can be joined in a *thorium subfamily* (Th—Cm) and the remaining seven in a *berkelium subfamily* (Bk—Lr).

In accordance with what we have said, the highest oxidation state of the actinides rises at first, then gradually falls:

Th	**Pa**	**U**	**Np**	**Pu**	**Am**	**Cm**
+4	+5	+6	+7	+7	+7	+4
Bk	**Cf**	**Es**	**Fm**	**Md**	**No**	**Lr**
+4	+3	+3	+3	+3	+3	+3

The stability of the lowest oxidation state, +2, increases in the Cf—No series (according to Spitsin *et al.*) The coordination numbers of the actinides are quite varied (from four to twelve).

2.1. The Actinide Family

Thorium and uranium are dispersed elements, and protactinium is a rare one. The abundance of thorium in the crust is 7×10^{-5}, of uranium 2×10^{-5}, and of protactinium only 8×10^{-12} mole per cent. Minerals rich in thorium or uranium are seldom found; those found include *thorite* $ThSiO_4$ and *uranite* UO_{2-3}. Protactinium occurs with uranium.

The simple substances. As simple substances, thorium, protactinium, uranium, neptunium, plutonium, americium, and curium are silvery-white metals of high density, with relatively high melting and boiling points:

Metal	Th	Pa	U	Np	Pu	Am	Cm
Density, g/cm³	11.7	15.4	19.0	20.4	19.7	11.9	13.5
M.p., °C	1750	1575	1133	637	640	1200	1340
B.p., °C	4200	4300	3860	3900	3235	2600	

The simple substances of the actinides are very active. Most of them are gradually oxidised by oxygen and nitrogen. The metals burn in oxygen to form compounds corresponding to their stablest

oxidation states: e.g.

$$Th + O_2 = \overset{+4}{ThO_2}$$

$$4Pa + 5O_2 = 2\overset{+5}{Pa_2O_5}$$

$$3U + 4O_2 = U_3O_8\ (\overset{+4}{UO_2} \cdot 2\overset{+6}{UO_3})$$

$$Pu + O_2 = \overset{+4}{PuO_2}$$

Actinides react, when heated, with most of the other nonmetals. The resulting compounds have high heats of formation. Thorium, uranium, and other actinides can absorb large amounts of hydrogen, forming hydrides of variable composition (between EH_3 and EH_4). With metals actinides form alloys containing intermetallic compounds. The actinides stand much above hydrogen in the electromotive series and are therefore oxidised by water and even more so by acids. In normal conditions they do not react with alkalis.

Since they are very reactive, actinides are obtained by electrolysis of molten compounds, by metallothermic techniques, and by thermal decomposition of their compounds in deep vacuum at high temperatures. Thus, U and Th are isolated by electrolysing their molten complex fluorides (usually KEF_5); Th, Np, Pu, Am and Cm are obtained by reducing their fluorides with vapours of barium or sodium

$$NpF_4 + 2Ba = Np + 2BaF_2$$

while Pa is obtained by thermal decomposition of its compounds

$$2PaCl_5 = 2Pa + 5Cl_2$$

Berkelium Bk, californium Cf, einsteinium Es, fermium Fm, mendelevium Md, nobelium No, and lawrencium Lr have been synthesised in such tiny doses that adequate quantities have not been obtained in the metallic state. Their physical and chemical properties have therefore not been much studied, but are apparently similar to those of the lanthanides.

The uses of the actinides and their compounds are mainly connected with the problem of employing intratomic energy. Thorium also presents interest as an alloying additive for obtaining heat-resistant alloys.

2.2. Compounds of Actinides

Actinide(III) compounds. All actinides have a +3 oxidation state, but it is not characteristic of the first elements of the family (Th—Pu), in particular of Th and Pa, and their few compounds are only stable as solids.

Actinide(III) compounds (provided their differences in oxidation-reduction activity are ignored) are quite similar to each other and

to the corresponding lanthanide(III) compounds. The similarity in chemical behaviour of lanthanide(III) and actinide(III) ions in aqueous solutions is seen, for example, in their ion exchange separation. A similarity of crystal structure, solubility, character of hydrolysis, composition of crystal hydrates, and other properties has also been observed in compounds of the same type in the solid state.

The *hydroxides* of actinides $E(OH)_3$, like those of lanthanides(III), are barely soluble in water and display marked basic properties. In particular, they react readily with acids.

Of the compounds of these elements, $E(NO_3)_3$, ECl_3, EBr_3, EI_3 and $E_2(SO_4)_3$ are soluble in water, but EF_3, EPO_4, etc. are difficult to dissolve.

Compounds of Th(III), Pa(III), U(III), and Np(III) are powerful reducing agents and, for example, decompose water:

$$2UCl_3 + 4H_2O = 2U(OH)_2Cl_2 + H_2 + 2HCl$$

Derivatives of Pu(III) are less vigorous reducing agents but are readily oxidised in solution by atmospheric oxygen.

Actinide(IV) compounds. An oxidation state of +4 is most typical of thorium and plutonium; it is also observed with protactinium, uranium, neptunium, americium, and curium.

Actinides(IV) are similar to each other chemically, and to cerium(IV) and group IV *d* elements (the titanium subgroup).

Isomorphous crystalline oxides are known for actinides(IV): white ThO_2, brown-black PaO_2, brown UO_2, yellow NpO_2, and black AmO_2. Some are high-melting (the melting point of ThO_2, for example, is 3050 °C and of UO_2 2176 °C). EO_2 are practically insoluble in water and do not react with it chemically; they also do not dissolve in dilute acids. Nor does it react with alkalis (even by fusing).

$E(OH)_4$ hydroxides, obtained by exchange reactions, display rather weak basic properties.

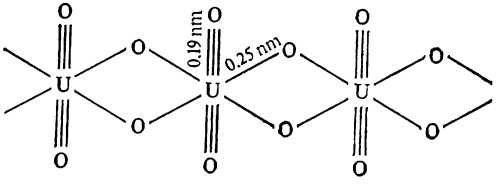
Of the actinide(IV) compounds, the nitrates are readily soluble in water, the sulphates moderately so, and the phosphates, carbonates, iodates, etc., only slightly. The soluble compounds are strongly hydrolysed.

The crystal hydrates of the actinides(IV) usually contain from four to twelve molecules of water, e.g. $Th(NO_3)_4 \cdot 4H_2O$, $Th(NO_3)_4 \cdot 12H_2O$, $Th(SO_4)_2 \cdot 4H_2O$. The derivatives of actinide(IV) anion complexes are also quite characteristic, for example, $K[Th(NO_3)_5]$, $K_4[Th(SO_4)_4(OH_2)_2]$, K_2EF_6.

$EHal_4$ tetrahalides are known for all actinides of the thorium subfamily. They are quite high-melting and barely soluble in water. Tetrachlorides have been obtained for Th, Pa, U, and Np; only tetrabromides and tetraiodides are known for Th, U, and Np.

Actinide(IV) compounds have a complicated structure and high coordination numbers (six to twelve).

tened UO_6 octahedra joined along common edges into chains of a $[(UO_2)O_2]^{2-}$ composition



with Mg^{2+} ions between them.

In hydroxides of H_2EO_4 composition basic properties predominate over acidic ones; by chemical behaviour they can be regarded as bases of an $EO_2(OH)_2$ type. These hydroxides react quite readily with acids to form derivatives of EO_2^{2+} actinyl cations, for example

$$EO_2(OH)_2 + 2HNO_3 = EO_2(NO_3)_2 + 2H_2O$$

Similar derivatives are formed when UO_3 reacts with acids

$$UO_3 + 2HCl = UO_2Cl_2 + H_2O$$

Most derivatives of EO_2^{2+} crystallise easily and are readily soluble in water, being salts and salt-like compounds. The hydrolysis of EO_2^{2+} is reversible:

$$UO_2(NO_3)_2 + 2H_2O \rightleftarrows UO_2(OH)_2 + 2HNO_3$$

Uranyl nitrate $UO_2(NO_3)_2$ is the most commonly used preparation of uranium in chemistry.

The acidic attributes of H_2EO_4 are only displayed during their fusion with alkalis

$$H_2EO_4 + 2KOH = K_2EO_4 + 2H_2O$$

The uranates(VI), neptunates(VI), and plutonates(VI) thus obtained are unstable and are decomposed by water.

The stability of E(VI) compounds diminishes in the U—Np—Pu—Am series. A stable orange oxide UO_3 has been obtained for uranium, for instance, only the mixed neptunium(VI) oxide Np_3O_8—neptunium(IV) neptunate(VI) $Np(NpO_4)_2$—for neptunium, while no oxide of plutonium(VI) has been obtained at all. In the same way stability declines in the fluorides. UF_6 and NpF_6 are more or less stable volatile substances, while PuF_6 is unstable. Of the other halides, only UCl_6 is comparatively stable; chlorides of Np(VI) and Pu(VI) have not been obtained, nor have bromides or iodides ever been obtained for U(VI).

The derivatives of Np(VI) and especially of Pu(VI) and Am(VI) are powerful oxidants:

$$2NpO_2Cl_2 + SnCl_2 = 2NpO_2Cl + SnCl_4$$

Actinide(VII) compounds. Compounds of neptunium (VII) and plutonium(VII) are formed by the reaction of active oxidants (O_3, ClO^-, BrO^-) with strongly alkaline solution of oxyneptunates(VI) and oxyplutonates(VI), e.g.:

$$2NpO_5^{3-} + O_3 + 2OH^- = 2NpO_5^{3-} + O_2 + H_2O$$

Oxyneptunates(VII) and oxyplutonates(VII) of the type of $Ba_3(NpO_5)_2 \cdot nH_2O$ and $Ba_3(PuO_5)_2 \cdot nH_2O$, $[Co(NH_3)_6]NpO_5 \cdot 3H_2O$, etc., can be obtained from these solutions. The derivatives of NpO_5^{3-} are dark green and those of PuO_5^{3-} brownish-black. A brownish-black hydroxide with a $NpO_2(OH)_3$ composition has also been precipitated. The hydroxide has amphoteric properties, is readily soluble in alkalis, yielding green solutions (NpO_5^{3-} ion), and in acids, forming yellow-brown solutions (NpO_2^{3+} ion). In an acidic solution, however, compounds of Np(VII) are rapidly converted into Np(VI) ones. Compounds of Am(VII) have been obtained. The +7 oxidation state of actinides was first discovered by the Soviet chemists Krot, Gelman *et al.*

Derivatives of neptunium(VII), and especially of plutonium(VII) and americium(VII), are strong oxidants. Derivatives of Np(VIII) and Pu(VIII) have also been reported.

The derivatives of Am(IV) and Cm(IV) are strong oxidants, and can oxidise, for example, concentrated hydrochloric acid:

$$2AmO_2 + 8HCl = 2AmCl_3 + Cl_2 + 4H_2O$$

Strong reducing agents, like nascent hydrogen, are required to reduce compounds of U(IV) and Np(IV), but even weak oxidants like I_2, Fe^{3+}, and HNO_3 can transfer U(IV) and Np(IV) to higher oxidation states:

$$3UO_2 + 8HNO_3 = 3UO_2(NO_3)_2 + 2NO + 4H_2O$$

$$2Np(NO_3)_4 + I_2 + 4H_2O = 2NpO_2NO_3 + 6HNO_3 + 2HI$$

Actinide(V) compounds. The oxidation state of +5 is most stable for protactinium and neptunium, and is met less often in plutonium compounds. Actinides(V) behave like *d* elements and a similarity with elements of the vanadium subgroup has been observed. In contrast to them, however, actinide(V) compounds of the same type display stronger basic properties.

Pa_2O_5, for instance, in practice does not display acidic properties even when fused with soda; on the contrary, it is markedly soluble in hot sulphuric acid:

$$Pa_2O_5 + H_2SO_4 = (PaO_2)_2SO_4 + H_2O$$

The same can be said of protactinium(V) hydroxide (average composition $HPaO_3$). It is insoluble in water, and chemically is a weak base of the $PaO_2(OH)$ type, with certain acidic properties; it reacts comparatively easily with acids, for instance, to form derivatives of the PaO_2^+ (*protactinyl*) radical:

$$PaO_2(OH) + HCl = PaO_2Cl + H_2O$$

The acidic properties of $HPaO_3$ are so weakly expressed that stable *protactinates*(V) cannot be obtained even by fusing it with alkalis.

The oxides and hydroxides of uranium(V), neptunium(V), and plutonium(V) behave in a similar way. The compounds of these elements most stable in aqueous solutions are derivatives of complex cations of the EO_2^+ type, for example, UO_2Cl, NpO_2F, and PuO_2Cl.

The following derivatives of actinides(V) have been isolated in the free state: the fluorides PaF_5, UF_5, NpF_5, the chlorides $PaCl_5$ and UCl_5, the bromide $PaBr_5$, and certain others. All are volatile and almost completely hydrolysed in aqueous solutions:

$$PaCl_5 + 3H_2O \rightleftharpoons HPaO_3 + 5HCl$$

Derivatives of anion complexes deserving mention are the complex fluorides of $M[EF_6]$ type, which resemble double salts in their solubility.

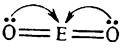
There are few compounds of Am(V) and Pu(V); they display oxidising properties:

$$2AmO_2F + 2H_2O_2 + 3H_2SO_4 = Am_2(SO_4)_3 + 2O_2 + 2HF + 4H_2O$$

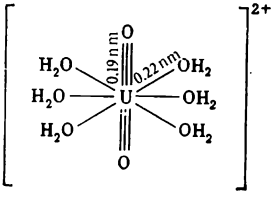
Actinide(VI) compounds. A +6 oxidation state is most characteristic of uranium, and can also be observed with neptunium and plutonium, but less frequently with americium. In this oxidation state, the actinides resemble group VI *d* elements (the chromium subgroup).

Many of the compounds of uranium and other actinides in the highest E(V) and E(VI) oxidation states include EO_2^+ and EO_2^{2+} atom groups known as *actinyls* that remain unaltered in various chemical reactions: UO_2^{2+} *uranyl*, NpO_2^{2+} *neptunyl*, PaO_2^+ *protactinyl*, etc.

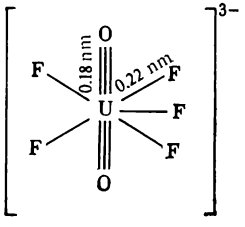
The special stability of these groups is due to the presence of a triple bond between the actinide and oxygen atoms. Two of these bonds are formed by two unpaired electrons each of the actinide and oxygen atoms, while the third is formed by an unshared electron pair of the oxygen atom and a free orbital of the actinide atom:



The actinyl atom group forms part both of cation and of anion complexes with a bipyramid structure (hexagonal, pentagonal, and tetragonal). The OEO group on the vertical axis of the bipyramid has a short EO bond length; the bond lengths between the actinide atoms and the other atoms in the equatorial plane are longer. These complexes can therefore be considered to contain an EO_2 group with strong EO bonds, to which the other atoms, or groups of atoms, are joined by a weaker interaction. Yellow crystalline $UO_2(NO_3)_2 \cdot 6H_2O$, for example, has an insular structure and consists of $UO_2(OH_2)_6^{2+}$ and NO_3^- ions. The $UO_2(OH_2)_6^{2+}$ complex has a hexagonal bipyramidal structure with the uranium atom at the centre:



The structure of $K_2[UO_2F_5]$ is of an insular type consisting of K^+ and $UO_2F_5^{3-}$ ions. The latter are pentagonal bipyramids with the uranium atom at the centre. The oxygen atoms are located on the vertical (quintuple) axis of the bipyramid:



Many other compounds of the highest oxidation states of actinides have similar structures. The UO_2F_2 unit cell, for instance, is a hexagonal bipyramid UO_2F_6 that forms planar polymeric layers of UO_2F_2 in which the oxygen atoms are located above and below the layers. The crystals of $MgUO_4$ consist of flat

V

TRANSMUTATION OF CHEMICAL ELEMENTS

CHAPTER 1

Radioactivity

The first step in scientific solution of the transmutation of elements was Becquerel's discovery of the radioactivity of uranium in 1896. Two years later Marie Sklodowska-Curie and Pierre Curie discovered radioactivity in thorium, and two new radioactive elements, polonium and radium. The explanation of radioactivity as the result of nuclear fission (Rutherford and Soddy, 1903) indicated that the chemical elements are not eternally immutable and can be transformed into one another; from that moment the business of artificially transmuting elements received a firm scientific foundation. The laws of the transmutation of the nuclei of elements are studied by *nuclear chemistry*.

The life of atoms depends on the structure of their nuclei and is characterised by a *half-life* $T_{1/2}$, i.e. the time taken for half of the nuclei of a given radioactive element to disintegrate. The half-life of the various radioactive elements varies within very wide limits, from thousandths of a second to thousands of millions of years. Most isotopes have half-lives between 30 seconds and ten days. It seems that an element can be found in terrestrial conditions when it 'outlives' the 4500 to 5000 million years of the planet or its stocks are continually replenished through appropriate nuclear transformations.

1.1. Nuclear Fission

The most frequent transformation process is *beta-decay*, in which the nucleus emits an electron (negative beta particle) through the transformation of one of its neutrons into a proton along the following line

$$n \rightarrow p + \beta^- + \tilde{\nu}$$

in which some of the energy liberated is carried away by an antineutrino $\tilde{\nu}$. The *neutrino* ν and *antineutrino* $\tilde{\nu}$ are elementary particles that have no charge and differ from each other only in spin.

It is not difficult to guess that the charge of the nucleus increases by one unit during β^- decay, while its mass number remains unaltered; in other words, an isotope with an atomic number one unit greater than that of the parent element is formed. During β^- decay

of thorium-234, for example, an isotope of protactinium-234 is formed, while polonium-210 is produced during β^- decay of bismuth-210:

$$^{234}_{90}\mathrm{Th} = {}^{234}_{91}\mathrm{Pa} + \beta^- + \tilde{\nu}$$

$$^{210}_{83}\mathrm{Bi} = {}^{210}_{84}\mathrm{Po} + \beta^- + \tilde{\nu}$$

Nuclei in which the number of neutrons is less than the number of protons are characterised by *positron decay*, i.e. decay accompanied by the emission of a *positron* (β^+ particle), a particle with a unit positive charge and the mass of the electron; β^+ decay is the result of the transmutation of a proton into a neutron:

$$p \rightarrow n + \beta^+ + \nu$$

During positron decay the charge of the nucleus is reduced by one unit while its mass number (as in β^- decay) does not change. An example is the transmutation of carbon-11 into the isotope boron-11:

$$^{11}_{6}\mathrm{C} \rightarrow {}^{11}_{5}\mathrm{B} + \beta^+ + \nu$$

A similar transformation of the nucleus occurs with *electron capture*, a phenomenon that consists in an electron being captured by the nucleus from one of the subshells lying closest to it. It is accompanied by the transmutation of a proton into a neutron

$$p + e^- \rightarrow n$$

for example,

$$^{40}_{19}\mathrm{K} + e^- \rightarrow {}^{40}_{18}\mathrm{Ar} + \gamma$$

The biggest changes in nuclei are observed in *alpha decay*. The emission of an α particle (a helium-4 nucleus) leads to the formation of an isotope of an element with a nuclear charge two units less than the parent element, while the mass number decreases by four units. Alpha decay is characteristic of heavy elements, like the uranium isotope U-234:

$$^{234}_{92}\mathrm{U} \rightarrow {}^{230}_{90}\mathrm{Th} + {}^{4}_{2}\mathrm{He}$$

All these types of radioactive transmutation are often accompanied with *gamma-radiation*, linked with transition of the newly formed nucleus from an excited state to its ground state.

Apart from natural α^- and β^- radioactivity, *spontaneous fission* of the nuclei of heavy elements into two parts is also possible. This phenomenon was first discovered in ^{238}U, and is characteristic of transuranium elements.

1.2. Radioactive Series

All elements after bismuth in the periodic system are radioactive. Among them there are only three nuclei, viz., thorium-232 ($T_{1/2}$ = 1.4×10^{10} years), uranium-235 ($T_{1/2} = 7 \times 10^8$ years), and

uranium-238 ($T_{1/2} = 4.5 \times 10^9$ years) whose life is sufficiently long for them to survive throughout the 4500 to 5000 million years of the world's existence. The other elements coming after bismuth in the periodic system are constantly being formed by the natural radioactive decay of ^{232}Th, ^{235}U, and ^{238}U nuclei.

The isotopes ^{232}Th, ^{238}U, and ^{235}U (also called *actinouranium*) begin three natural radioactive series of heavy elements known respectively as the *thorium*, *uranium* and *actinium series*. The alpha- or beta transformations of these series end in the formation of three stable isotopes of lead: ^{208}Pb, ^{207}Pb and ^{206}Pb (with a magic number of protons of 82). Since only alpha or beta decay takes place in these series, the mass numbers within each change either by four units at once or not at all. Only nuclei with mass numbers $A = 4n$, therefore, occur in the thorium series, nuclei with $A = 4n + 2$ in the uranium series, and nuclei with $A = 4n + 3$ in the actinium series (where n is a whole number between 51 and 59). A decay series with mass numbers $A = 4n + 1$ has not been found on the Earth.

The series of successive transformations in the uranium series ($A = 4n + 2$) is as follows:

$$^{238}_{92}\mathrm{U} \xrightarrow[4.5\times10^9\ \text{years}]{\alpha} {}^{234}_{90}\mathrm{Th} \xrightarrow[24.1\ \text{days}]{\beta^-} {}^{234}_{91}\mathrm{Pa} \xrightarrow[1.22\ \text{min}]{\beta^-}$$

$$\rightarrow {}^{234}_{92}\mathrm{U} \xrightarrow[2.67\times10^5\ \text{years}]{\alpha} {}^{230}_{90}\mathrm{Th} \xrightarrow[8\times10^4\ \text{years}]{\alpha} {}^{226}_{88}\mathrm{Ra} \xrightarrow[1622\ \text{years}]{\alpha}$$

$$\rightarrow {}^{222}_{86}\mathrm{Rn} \xrightarrow[3.823\ \text{days}]{\alpha} {}^{218}_{84}\mathrm{Po} \xrightarrow[3.05\ \text{min}]{\alpha} {}^{214}_{82}\mathrm{Pb} \xrightarrow[26.8\ \text{min}]{\beta^-}$$

$$\rightarrow {}^{214}_{83}\mathrm{Bi} \begin{cases} \xrightarrow[19.7\ \text{min}]{\alpha} {}^{210}_{81}\mathrm{Tl} \xrightarrow[1.32\ \text{min}]{\beta^-} \\ \xrightarrow[19.7\ \text{min}]{\beta^-} {}^{214}_{84}\mathrm{Po} \xrightarrow[1.5\times10^{-4}\ \text{s}]{\alpha} \end{cases} {}^{210}_{82}\mathrm{Pb} \xrightarrow[2.21\ \text{years}]{\beta^-}$$

$$\rightarrow {}^{210}_{83}\mathrm{Bi} \xrightarrow[5.02\ \text{years}]{\beta^-} {}^{210}_{84}\mathrm{Po} \xrightarrow[138\ \text{days}]{\alpha} {}^{206}_{82}\mathrm{Pb}\ (\text{stable})$$

Neptunium-237 isotope begins a radioactive series with $A = 4n + 1$, which consists of radioactive nuclei (including Fr and At) whose half-life does not exceed 1.6×10^5 years, which explains why they are not found on Earth. The end product of the disintegration of this series is the nonradioactive isotope of bismuth $^{209}_{83}$Bi (magic number of neutrons 126).

The radioactive isotopes can be obtained at present for any chemical element of the periodic system (through the appropriate nuclear reactions). Artificial radioactivity was discovered by Irene and Frederick Joliot-Curie (1934).

CHAPTER 2

Nuclear Reactions

By nuclear reactions is understood the interaction of various particles (neutrons, protons, deutrons, alpha-particles, and other atomic nuclei) with the nuclei of chemical elements. The simplest ones have the following mechanism. A bombarding particle is captured by the target nucleus and an intermediate composite nucleus formed with a very short life (about 10^{-7} second). This composite nucleus emits an elementary particle or a light nucleus and is transformed into a new nucleus.

The first artificial nuclear transformation was effected in 1919 by Rutherford, who converted nitrogen atoms into oxygen ones by bombarding them with alpha particles. The intermediate composite nucleus in this reaction was an isotope of fluorine $^{18}_{9}F$:

$$^{14}_{7}N + {}^{4}_{2}He \rightarrow (^{18}_{9}F) \rightarrow {}^{17}_{8}O + {}^{1}_{1}H \text{ or } {}^{14}_{7}N(\alpha, p){}^{17}_{8}O$$

In order to overcome the Coulomb repulsive forces of the nuclei, bombarding particles must clearly possess high energy. In recent years, experimental physicists, using various kinds of accelerators, have obtained particles with energies of the order of tens of giga electron volts (10 GeV). Such particles had only previously been observed in cosmic rays and in infinitesimal quantities. Examples of the nuclear reactions are as follows:

1. Reactions with bombardment by alpha particles ($^{4}_{2}He^{2+}$ ions)

$$^{14}_{7}N + {}^{4}_{2}He \rightarrow {}^{17}_{8}O + {}^{1}_{1}H \qquad {}^{14}_{7}N\,(\alpha, p)\,{}^{17}_{8}O$$
$$^{9}_{4}Be + {}^{4}_{2}He \rightarrow {}^{12}_{6}C + {}^{1}_{0}n \qquad {}^{9}_{4}Be\,(\alpha, n)\,{}^{12}_{6}C$$

The second reaction is a convenient means of obtaining neutrons.

2. Reactions with bombardment by protons ($^{1}_{1}H^{+}$ ions)

$$^{21}_{10}Ne + {}^{1}_{1}H \rightarrow {}^{18}_{9}F + {}^{4}_{2}He \qquad {}^{21}_{10}Ne\,(p, \alpha)\,{}^{18}_{9}F$$
$$^{63}_{29}Cu + {}^{1}_{1}H \rightarrow {}^{63}_{30}Zn + {}^{1}_{0}n \qquad {}^{63}_{29}Cu\,(p, n)\,{}^{63}_{30}Zn$$

3. Reactions with bombardment of deutrons ($^{2}_{1}H^{+}$ ions)

$$^{24}_{12}Mg + {}^{2}_{1}H \rightarrow {}^{22}_{11}Na + {}^{4}_{2}He \qquad {}^{24}_{12}Mg\,(d, \alpha)\,{}^{22}_{11}Na$$
$$^{41}_{19}K + {}^{2}_{1}H \rightarrow {}^{42}_{19}K + {}^{1}_{1}H \qquad {}^{41}_{19}K\,(d, p)\,{}^{42}_{19}K$$

4. Reactions with bombardment by neutrons

$$^{10}_{5}B + {}^{1}_{0}n \rightarrow {}^{7}_{3}Li + {}^{4}_{2}He \qquad {}^{10}_{5}B\,(n, \alpha)\,{}^{7}_{3}Li$$
$$^{59}_{27}Co + {}^{1}_{0}n \rightarrow {}^{60}_{27}Co + \gamma \qquad {}^{59}_{27}Co\,(n, \gamma)\,{}^{60}_{27}Co$$

5. Reactions with bombardment by photons (γ-rays)

$$^{63}_{29}Cu + \gamma \rightarrow {}^{62}_{29}Cu + {}^{1}_{0}n \qquad {}^{63}_{29}Cu\,(\gamma, n)\,{}^{62}_{29}Cu$$
$$^{27}_{13}Al + \gamma \rightarrow {}^{26}_{12}Mg + {}^{1}_{1}H \qquad {}^{27}_{13}Al\,(\gamma, p)\,{}^{26}_{12}Mg$$

The discovery of uranium fission under the action of thermal neutrons in 1939 played a decisive role in the development of nuclear chemistry:

$$^{235}_{92}U + ^{1}_{0}n \rightarrow ^{92}_{36}Kr + ^{141}_{56}Ba + 2^{1}_{0}n$$

During nuclear reactions, the nucleus is split into two new highly radioactive nuclei of unequal mass. The reaction is accompanied with the liberation of enormous energy; around 200 MeV are liberated, for example, in the reaction above (about 165 MeV through nuclear fission and around 35 MeV through radioactive decay of the fission products). An energy of 200 MeV is equivalent to 19.2×10^9 kJ/mol, or 8.4×10^{10} kJ/kg ^{235}U. This is equivalent to the heat of burning two million kilograms of high-calorific coal.

During fission, two or three new neutrons are formed per spent neutron; they, in turn, can induce nuclear fission in other nuclei. The number of split nuclei can thus increase like in an avalanche to cause a chain reaction. If the development of the chains is not controlled, the release of energy is explosive (the principle of the atomic bomb).

The operation of nuclear reactors is based on controlled chain reactions of the fission of nuclei of uranium (or plutonium). Fission in reactors is employed to generate energy, obtain transuranium elements, radioactive isotopes of other elements, and so on.

An important type of nuclear reaction is the thermonuclear reaction in which the atomic nuclei are fused into more complicated ones. An example is the synthesis of helium nuclei from the nuclei of hydrogen (protons):

$$4^{1}_{1}H \rightarrow ^{4}_{2}He + 2\beta^{+}$$

Enormous energy is liberated in thermonuclear reactions (see p 17). As with the synthesis of helium this energy is 6.87 MeV or 644 million kJ per gramme of hydrogen, which is three million times greater than the energy liberated by the combustion of hydrogen, and 15 million times greater than that liberated by burning of the same quantity of high-calorific coal.

Thermonuclear reactions can proceed only at very high temperatures (above a million degrees). High energy is imparted to colliding particles by the great heat within stars, during an atomic explosion, or in a powerful gas discharge. So far only uncontrollable thermonuclear reactions have been realised with an explosive liberation of energy (hydrogen bomb). The scheme of the reaction is as follows:

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{3}_{1}H$$
$$^{3}_{1}H + ^{2}_{1}H \rightarrow ^{4}_{2}He + ^{1}_{0}n$$
$$^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{1}H + ^{1}_{1}H$$
$$^{2}_{1}H + ^{2}_{1}H \rightarrow ^{3}_{2}He + ^{1}_{0}n$$

The temperatures (about 10^7 K) and neutrons needed for these reactions are created by the atomic explosion (of an atomic 'fuze'), i.e. a chain reaction of the splitting of nuclei of ^{235}U or ^{239}Pu. The energy liberated during the explosion of a hydrogen bomb is greater than a week's generation of electricity by the entire world, and is only comparable to the power of earthquakes or hurricanes.

At present scientists are working on the problem of controlled thermonuclear reactions. Its successful solution will enable humanity to utilise inexhaustible reserves of atomic energy.

Study of the laws of nuclear transformation is decisive for determining the properties of nuclei and the nature of nuclear forces, and for developing the theory of the structure of the atomic nucleus. Study of nuclear reactions is of great practical significance, above all for the employment of atomic energy for practical purposes, and for obtaining new chemical elements, various radioactive isotopes, etc., artificially. The development of means for accelerating particles has made it possible to get conditions in the laboratory close to phenomena occurring in the Earth's crust and in outer space, and to clarify the genesis of elements in nature.

2.1. Synthesis of Elements

In 1869, when Mendeleev discovered the periodic law, only 63 elements were known. On the basis of his law, Mendeleev predicted the existence of twelve new elements, the physical and chemical properties of three of which (Ga, Ge, Sc) he described exactly. In the half-century between 1875 and 1925 almost all the elements in the periodic system before uranium had been found in nature. The periodic law and the method of prediction suggested by Mendeleev guided research workers in their search for, and prediction of the chemical nature, of new elements.

By 1925, only the elements with atomic numbers 43, 61, 85, and 87, which (as appeared later) do not form stable isotopes, remained undiscovered.

The first of them to be obtained synthetically was element 43, technetium (Tc), which prior to 1937 had filled the space in the periodic table between molybdenum and ruthenium. Technetium was first obtained by bombarding molybdenum with deutrons:

$$^{98}_{42}\mathrm{Mo} + {}^{2}_{1}\mathrm{H} \rightarrow {}^{92}_{43}\mathrm{Tc} + {}^{1}_{0}n \text{ or } {}^{98}_{42}\mathrm{Mo}\,(d,\ n)\,{}^{99}_{43}\mathrm{Tc}$$

In 1940 element 85, astatine At, was obtained by irradiating bismuth with alpha particles:

$$^{209}_{83}\mathrm{Bi} + {}^{4}_{2}\mathrm{He} \rightarrow {}^{211}_{85}\mathrm{At} + 2{}^{1}_{0}n \text{ or } {}^{209}_{83}\mathrm{Bi}\,(\alpha,\ 2n)\,{}^{211}_{85}\mathrm{At}$$

Elements 61 (promethium Pm) and 87 (francium Fr) were discovered among the breakdown products of uranium decay.

To synthesise transuranium elements, reactions are employed, involving neutrons, alpha particles, and deutrons with energies of the order of 30 to 40 MeV, and multicharge ions ($^{10}B^{3+}$, $^{12}C^{4+}$, $^{14}N^{5+}$, $^{16}O^{6+}$, $^{22}Ne^{10+}$) with energies to 130 MeV.

The advances in the synthesis and study of transuranium elements are mainly connected with the work of American scientists at the University of California (Berkeley) headed by Glenn Seaborg and scientists of the socialist countries led by G. N. Flerov at the Joint Institute for Nuclear Research in Dubna (USSR).

By long bombardment of uranium-238 ($Z = 92$) by a flux of neutrons in a nuclear reactor it is possible to obtain isotopes of all transuranium elements up to fermium Fm ($Z = 100$). The isotope ^{239}U is initially produced, which turns into the neptunium ^{239}Np isotope through β^- decay ($Z = 93$). The neptunium isotope passes in the same way into an isotope of plutonium ^{239}Pu ($Z = 94$):

$$^{238}_{92}U\ (n,\ \gamma)\ ^{239}_{92}U \xrightarrow{-\beta^-} {}^{239}_{93}Np \xrightarrow{-\beta^-} {}^{239}_{94}Pu$$

The plutonium isotopes can, in turn, absorb neutrons and the chain of (n, γ) reactions and β^- decay can be continued until fermium is formed ($Z = 100$):

$$^{239}_{94}Pu\ (4n,\ 4\gamma)\ ^{243}_{94}Pu \xrightarrow{-\beta^-} {}^{243}_{95}Am\ (n,\ \gamma)\ ^{244}_{95}Am \xrightarrow{-\beta^-} {}^{244}_{96}Cm \rightarrow \ldots$$

$$\ldots \rightarrow {}^{255}_{99}Es \xrightarrow{-\beta^-} {}^{255}_{100}Fm\ (n,\ \gamma)\ ^{256}_{100}Fm \rightarrow \text{spontaneous decay}$$

The heaviest artificial elements can be obtained by reactions involving alpha particles and multicharge ions in powerful accelerators, for example:

$$^{238}_{92}U\ (^{14}N,\ 6n)\ ^{246}_{98}Es$$

$$^{238}_{92}U\ (^{16}O,\ 4n)\ ^{250}_{100}Fm$$

$$^{253}_{99}Es\ (\alpha,\ n)\ ^{256}_{101}Md$$

In 1964, a group headed by G. N. Flerov obtained an isotope of element 104 through bombarding plutonium-242 ($Z = 94$) by nuclei of neon-22 ($Z = 10$) in a powerful accelerator:

$$^{242}_{94}Pu + ^{22}_{10}Ne \rightarrow {}^{260}_{104}Ku + 4n$$

They proposed calling the new element kurchatovium in honour of the outstanding Soviet nuclear physicist I. V. Kurchatov.

In 1967, the first nuclei of element 105 were synthesised in Dubna by bombarding americium-243 ($Z = 95$) by nuclei of neon-22 ($Z = 10$) with an energy of the order of 120 MeV:

$$^{243}_{95}Am + ^{22}_{10}Ne \rightarrow {}^{260}105\ (^{261}105) + 5^1_0n\ (4^1_0n)$$

Elements 106 and 107 have been synthesised by bombarding lead isotopes with chromium-54 and manganese-55 ions.

2.2. The Outlook for the Synthesis of New Elements

The half-life of transuranium elements decreases rapidly with growth of the nuclear charge. The most stable isotope of Pu has a half-life of 70 million years, of Bk 7000 years, of Es two years, and of Md 80 days. For Ku isotopes the half-life is between 70 seconds and 0.1 second, Ns between 40 and 1.5 seconds, and for element 106 between 1.0 and 0.007 second.

Since there is a steady decrease in the half-lives of elements, we might expect the lower limit of the periodic system to be attained in the region of elements 106 or 108, but there are important theoretical grounds for suggesting that there should be nuclei among the superheavy elements with closed nucleon layers of increased stability corresponding to 'magic' numbers of protons, $Z = 114$ and 126, and of neutrons $N = 184$. It has been calculated that nuclei with double 'magic' numbers, like $^{298}_{114}$E (114p, 184n) and $^{310}_{126}$E (126p, 184n) would have half-lives of 10^6 to 10^7 years. In that case it would be logical to search for practical ways of synthesising elements with atomic numbers around 114 and to try and discover elements 110 and 114 in nature.

Elements 114 and 126 might be synthesised in two ways. The first is to employ a fusion reaction with heavy ions, e.g.

$$_{94}\mathrm{Pu} + {}_{20}\mathrm{Ca} \rightarrow (114) + xn$$

$$_{90}\mathrm{Th} + {}_{36}\mathrm{Kr} \rightarrow (126) + xn$$

The other is to induce fusion of uranium nuclei with uranium nuclei, which would yield composite nuclei, whose subsequent fission would give fragments which might be the nuclei of transuranium elements.

The development of the physics and chemistry of transuranium elements is based directly on Mendeleev's periodic law. Study of the transuranium elements, in turn, is deepening our knowledge of the structure and properties of atomic nuclei, and widening our concepts of the structure of the periodic system. Despite the enormous advances made in science over the past century, the system proposed by Mendeleev has not undergone any substantial change, and the development of our concepts of the periodic system has in fact only concerned extension of its lower limits.

2.3. Nuclear Reactions in Nature

Study of the laws of nuclear reactions and radioactive decay has made it possible to pose the development of a theory of the origin and occurrence of the chemical elements in nature. The current findings of nuclear physics and astrophysics indicate that the synthesis and transmutation of elements occur at all stages of the evolution of stars as the regular process of their development.

Nuclei of complicated composition may be formed in nature either by the fusion of charged particles (elementary particles or atomic

nuclei), or by reactions associated with the absorption of neutrons. The conditions required for such reactions are found either in the interior of stars of various types (where charged particles are accelerated at high temperatures of the order of hundreds of million degrees) or in stellar atmospheres in which particles are accelerated by powerful electromagnetic fields.

At ten to twenty million degrees, nuclear reactions begin transmuting hydrogen into helium according to the following general scheme:

$$4{}_1^1\mathrm{H} \rightarrow {}_2^4\mathrm{He} + 2\beta^+$$

This reaction is the main source of the enormous energy that maintains the Sun and most stars in an incandescent state.

In stars of other types and age, thermonuclear reactions of helium occur at temperatures above 150 million degrees, which yield stable isotopes of carbon, oxygen, neon, magnesium, sulphur, argon, calcium, etc.:

$$^4\mathrm{He}(\alpha, \gamma)^8\mathrm{Be}(\alpha, \gamma)^{12}\mathrm{C}(\alpha, \gamma)^{16}\mathrm{O}(\alpha, \gamma)^{20}\mathrm{Ne}(\alpha, \gamma)^{24}\mathrm{Mg}$$

Reactions involving protons and neutrons also take place and elements up to and including bismuth are produced.

The very heaviest elements—uranium, thorium, and transuranium elements—are produced in the explosions of supernovae, with the release of enormous energy and a rise of temperature to around 4000 million degrees, which provides conditions for the formation of the heaviest elements.

These high temperatures cannot be generated inside planets; consequently the nuclear reactions that occur in them cannot be as diverse as those in hot stars. The transmutation of elements on the Earth comes about mainly through radioactive decay, which alters the isotopic composition of the existing elements slightly (25 per cent of which are radioactive).

Infinitesimal amounts of certain elements, that were first synthesised in the laboratory, have been found on the Earth (neptunium, plutonium, technetium, etc.). They may once have existed in considerable quantity but, owing to their instability, they have disappeared and are now formed only by nuclear reactions induced by cosmic radiation, or occur as products of the radioactive decay of other elements.

Elements with atomic numbers around 114 are expected to be found in terrestrial conditions.

The chemical element, like all nature, from the minutest particles to the largest bodies, from a grain of sand to the Sun, is thus in a state of 'eternal coming into being and passing away, in ceaseless flux, in unresting motion and change'.*

* Frederick Engels. *Dialectics of Nature*. Translated by Clemens Dutt, with a preface and notes by J.B.S. Haldane, F.R.S. (Lawrence & Wishart, London, 1940), p. 13.

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NAME INDEX

Andrianov, 423
Arbuzov, 383
Arrhenius, 135
Avogadro, 16
Azizova, 5

Badygina, 5
Balmer, 23, 24
Becquerel, 654
Beketov, 249
Belov, 160
Berthollet, 214, 268, 298
Biron, 48
Block, 155
Bohr, 15
Born, 175
Broglie, 19
Butlerov, 50, 232

Chernyaev, 101, 613
Chugaev, 101
Clarke, 232

Dalton, 268
Debye, 91

Einstein, 17, 18
Engels, 13, 147, 166, 662

Fersman, 232
Feuerbach, 147, 166
Flerov, 660

Galilei, 106
Gelman, 653
Gibbs, 166
Glauber, 490
Goldschmidt, 160, 232
Grinberg, 101
Guldberg, 185

Haber, 175
Heisenberg, 19
Heitler, 55
Hess, 169, 170, 173, 176
Hinshelwood, 208
Hund, 30, 55

Joliot-Curie, 656

Kablukov, 135
Kapustinsky, 131
Kistyakovsky, 135
Krot, 653
Kurchatov, 660
Kurnakov, 142, 268

Landau, 131
Lebedinsky, 101
Le Chatelier, 187, 218, 354
Lenin, 5, 50, 232
Lomonosov, 138, 142
London, 55
Lyman, 23, 24

Marx, 13
Mendeleev, 5, 15, 29, 30, 37, 134, 135, 137, 142, 149, 569, 659, 661
Mohr, 584
Moseley, 149
Mössbauer, 155, 157
Mulliken, 45, 55

Nernst, 225

Paschen, 23
Pauli, 29, 31, 56, 62
Pauling, 45, 55, 160
Planck, 18
Purcell, 155

Raoult, 138
Rutherford, 15, 656, 664

Schrödinger, 20, 50, 51, 55
Seaborg, 660
Semyonov, 14, 166, 208
Shchukarev, 48
Sklodowska-Curie, 654
Sleter, 55
Soddy, 664

Trofimuk, 269

Van der Waals, 98, 130
van't Hoff, 205
Vernadsky, 232
Vinogradov, 232, 237

Waage, 185
Wood, 385
Werner, 101

Zavoisky, 155

SUBJECT INDEX

Absolute electron charge, 88
Acids, 139
Actinides, 637
Actinium, 524
Activated complex, 202
Activation energy, 202
Activity coefficient, 190
Alabaster, 484
Alaite, 540
Albite, 458
Allotropes, 239
Allotropy, 118
Alnico, 606
Alumina, 455
Alumina gel, 456
Aluminium, 452
Aluminothermy, 453
Amblygonite, 487
Ammonia, 350
Ammonia water, 355
Amorphous state, 129
Amphitole, 420
Analysis, methods of, 142
Anorthite, 458
Anti-matter, 132
Antimonite, 383
Antimony, 383
Antimony glance, 383
Aquamarine, 472
Aqua regia, 361
Aquo complexes, 136
Argon, 497
Arsenic, 383
Arsenopyrite, 383
Asbestos, 420
Atomic heat of formation, 174
Atomic mass unit, 16
Atomic orbitals, 23
Atomic radii, 160
Atomic spectra, 24
Auripigment, 383
Austenite, 581
Autoionisation, 195
Autoprotolysis, 195
Autoprotolysis constant, 196
Avogadro's constant, 16

Baddeleyite, 529
Baking soda, 491
Balmer series, 23, 24
Barium, 481
Baryta water, 483
Baryte, 481
Bases, 139
Bauxite, 452
Bentonite, 420
Berlin blue, 587
Bertholide compounds, 268
Berthollet's salt, 298
Beryl, 420, 472
Beryllium, 472
Beryllium bronzes, 473
Binary compounds, 253
  acid-base properties of, 257
  stability of, 256
Bischofite, 479
Bismuth, 383
Bismuth glance, 383
Bismuthinite, 383
Bond, 50
  energy of, 50, 59, 173
  length and order of, 50, 59
  polarizability of, 88
Boranes, 442
Borax, 437
Borazon, 442
Born-Haber cycle, 175
Boron, 437
Boundary surface, 21

Cadmium, 628
Caesium, 492
Calcite, 481
Calcium, 481
Calomel, 630
Carbin, 395, 397
Carbon, 394
Carborundum, 442
Carnallite, 292, 478, 492
Cassiterite, 424
Catalysis, 211, 213
Celestine, 481
Cementite, 581

Cements, 480, 484
Chain reaction, 207
  branching, 208
Chalcopyrite, 117, 265, 619
Chalk, 481
Chemical bond, 74
Chemical conversion, physical stimulation of, 208
Chemical elements, abundance of, 232 233
Chemical equilibrium, 184
Chemical reactions, mechanisms of, 205
Chile nitre, 312
Chile saltpetre, 348
Chlorine, 291
Chlorophyll, 104
Chromite, 549
Chromium, 548
Cinnabar, 629
Clarke, 232
Clathrates, 268
Cobalt, 592
Cobalte glance, 592
Cobaltite, 592
Columbite, 540
Comparison of molecular-orbital, valence bond and crystal field theories, 515
Complexes
  anion, 102
  cation, 102
  classification of, 102
  colour of, 518
  high- and low-spin, 508
  formation of, 101
  neutral, 102
Complexing agents, 101
Conductors, 123
Coordination compounds, 505
Coordination isomerism, 523
Copper, 617
Copper glance, 619
Corundum, 454
Covalent bond, direction of, 77
Covalent crystals, 124
Covalent molecules, 90
Cristobalite, 419
Cryohydrates, 144
Cryolite, 287, 452, 490
Cryoscopic constant, 138
Crystal field theory, 505
Crystal lattice
  atomic, 108
  molecular, 108
Crystals, 106
Cuprite, 619
Daltonide compounds, 396
Deby unit, 91
Deformational polarization, 164
Degenerate orbitals, 26
Delocalized bond, 85
Deuterium, 278
Diamagnetism, 162
Diamond, 396
Diatomic homonuclear molecules, 58
Diffraction analysis, 158, 160
Diopside, 420
Dipole, 91
  induced, 94
  instantaneous, 93
  length of, 91
  moment, 93
    study of, 164
Dispersed systems, 132
Disproportionation, 225
Dissociation, 89
Dolomite, 477
Donor-acceptor interaction, 98, 136
  mechanism, 75
Duralumin, 454
Dzhezkazganite, 568

Ebullioscopic constant, 138
Effective charge, 88, 150
Effective concentration, 189
Electrode potential, 225
Electrolytic dissociation, 135
Electromagnetic spectrum, 147
Electron, 16
Electron affinity, 39, 43
Electron cloud, 20
Electron configuration of elements, 31
Electronegativity, 39, 45
Electron shell of atoms, 18
Electron structure of atoms, 29
Elements, scattered, 233
Emerald, 472
Endothermic process, 168
Energy, absorption and emission of, 18
Energy bond, 122
Energy levels, 23
Enstatite, 420
Enthalpy, 167, 168, 170
Entropy, 177
Entropy of activation, 204
Entropy factor, 180
Equilibrium concentration, 185, 186
Equilibrium constant, 196
Eutectic mixtures, 142, 143
Eutectics, 265
Excited states, 23

Exochemistry, 232
Exothermic process, 168

Feldspar, 458
Ferrite, 581
Field, 13
Fission, 655
Flint, 421
Fluorapatite, 287, 369
Fluorine, 286
Fluorite, 481
Fluorspar, 287
Forbidden band, 123
Force constant, 153
Free energy, 180
Freon, 404
Fuel cell, 230

Galena, 424
Gallium, 464
Gamma-ray spectroscopy, 155
Gaseous solution, 133
Gaseous state, 129
Gas hydrate, 268
Gell, 422
Germanium, 424
German silver, 620
Gibbs' free energy, 166, 180
Glass, 421
Glauber's salt, 490
Greenockite, 629
Gold, 617
Graphite, 396
Ground state, 23

Haematite, 580
Haemoglobin, 104
Hafnium, 528
Halite, 490
Hardness of water, 485
Heat of hydration of ions, 176
Helium, 496
Hess' law, 119, 173, 176
Hund rule, 30, 62
Hybridisation theory, 78
Hydrates, 134
Hydrogen, 277
Hydrogen bond, 99, 278
Hydrogen electrode, 226
Hydrogoethite, 580
Hydrolysis, 215
Hydrorgillite, 455
Hydroxyapatite, 369
Hydroxy aquo complex, 220
Hyperonic state, 131
Hyperons, 131
Hypervalency, 275
'Hypo', 338

Ilmenite, 117, 266, 529
Inclusion compounds, 268
Inconel, 606
Indian saltpetre, 348
Indium, 484
Infrared spectroscopy, 153
Instability constant, 193
Interaction between molecules, 97
Intermetallic compounds, 259, 261
  composition and structure of, 262
Internal energy, 167
Invar, 606
Inversion, 62
Ion exchangers, 455
Ionic bonds, 94
Ionic crystals, 124
Ionic radii, 160
Ionic solvates, 136
Ionisation, 89
  degree of, 135
  of acids and bases, 190, 192
Ionisation constant, 189
Ionisation energy, 39, 41
  of molecules, 64
Ionisation of isomerism, 523
Ion product, 195
Iridium, 592
Iron, 579
Isochoric process, 167

Kainite, 492
Kaolin, 453
Kernite, 437
Krypton, 498

Lanthanides, 636
Lanthanum, 524
Laser radiation, 209
Lattice energy, 175
Lautarite, 312
Law of mass action, 185
LCAO-MO method, 65
Lead, 425
Lead glance, 425
Le Chatelier's principle, 187, 218, 354
Lepidolite, 487
Ligands, classification of, 103
  spectrochemical series of, 515
Limestone, 481
Linear combination of atomic orbitals, 56
Liquid solutions, 134
Lithium, 487

Localized electron pairs, 74
  theory of, 82
Lyman series, 23, 24

Magic numbers, 17
Magnesite, 478
Magnesium, 477
Magnetic and electric fields, 162
Magnetic orbital quantum number, 25
Magnetic properties of molecules, 64
Magnetic spin quantum number, 29
Magnetite, 580
Malachite, 619
Manganese, 567
Marble, 481
Mass action law, 185, 190, 195
Mass defect, 17
Mass-energy equation, 17
Mass number, 17
Mechanochemistry, 210
Melchior, 620
Mercury, 628
Metallic bonds, 96
Metallochemistry, 259
Metallothermy, 249
Mica, 420, 458
Microfields, 13
Microparticles, 13
Mirabilite, 490
Mispikel, 383
Mixed compounds, 265
Mohr's salt, 584
Molecular crystals, 124
Molecularity of reaction, 200
Molecular orbitals, theory of, 55
Molecular sieves, 458
Molybdenite, 548
Molybdenum, 548
Monel metal, 606
Moseley's law, 149
Mössbauer effect, 155, 157
Multiple bonds, 84
Muscovite, 458

Neon, 497
Nepheline, 458
Nernst equation, 228
Neurons, 17
Neutrino, 655
Neutron, 16
Neutron state, 131
Nichromes, 606
Nickel, 604
Nimonic, 606
Niobium, 540
Nitrogen, 348
Nitrophoska, 381
Nonstoichiometric compounds, 207
Nonvalent types of bond, 94
Nuclear chemistry, 654
Nuclear fission, 655
Nuclear reaction, 657
Nucleon, 17
Nucleus, 16

Oleum, 339
Olivine, 477
Optical spectroscopy, 150
Orbital quantum number, 24
Orbitals, 21, 30
Orientation polarization, 164
Orpiment, 383
Orthoclase, 458
Osmium, 579
Other states of matter, 129, 131
Overlapping, 56
  zero, 61
Oxidation, 221
Oxidation number (state), 89
Oxidizing agent, 221
Oxygen, 314
Ozone, 315

Palladium, 604
Paramagnetic and diamagnetic substances, 64, 162
Partial pressure of gases, 133
Paschen series, 23
Passivation, 246
Patronite, 540
Pauling's scale, 45
Pauli's exclusion principle, 29, 31, 56, 58, 62
Periodicity of properties of elements, 39
Periodic law, 15
Periodic system, 29
  structure of, 37
Perovskite, 117, 266, 485, 529
Peroxides, 318
Peroxy acids, 322
Phase diagram, 143
Phenacite, 472
Phosphorite, 369
Phosphorus, 368
Photochemistry, 208
Photon, 19
Planck's constant, 18, 21
Plasma, 130
Plaster of Paris, 484
Platinite, 606
Platinum, 604

Polar and nonpolar molecules, 90
Polarity, 68
  of molecules, 92
Polonium, 341
Polymorphism, 118
Polynuclear complexes
  formation of, 219
Positron, 655
Potash, 495
Potassium, 492
Precipitated phosphate, 381
Principle quantum number, 23
Producer gas, 280
Protium, 278
Proton, 16
Prussian blue, 587
Pyrite, 331
Pyrolusite, 568
Pyrex glass, 450
Pyrometallurgy, 249
Pyroxenes, 420

Quanta, 18
Quantum mechanics, 18
Quantum number, 23
Quantum shell, 29
Quantum states, 23
Quartz, 419

Radial distribution of electron density, 27
Radiation chemistry, 210
Radii of atoms, 46
Radioactivity, 655
Radiolysis, 210
Radiospectroscopy 154
Radium, 481
Radon, 498
Raoult's law, 138
Reaction of simple substances to alkalis, 247
  dilute acids, 247
  oxidants, 247
  water, 246
Realgar, 383
Redox reactions, direction of, 225
Reducing agents, 221
Reduction, 221
Rhenium, 567
Rhodium, 592
Rock salt, 292, 490
Rubidium, 492
Ruthenium, 579
Rutile, 529

Sal ammoniac, 354
Salt bridge, 229
Sassolite, 437
Saturation of covalent bonds, 74
Scandium, 524
Scheelite, 549
Schrödinger equation, 21, 50, 51, 55
Screening, 34, 41
Secondary periodicity, 48
Selenium, 344
Selenochemistry, 233
Semiconductors, 123
Shell structure, 1
Siderite, 580
Silanes, 418
Silica, 419
Silica gel, 422
Silicon, 412
Silumin, 454
Silver, 617
Smithstone, 629
Soda ash, 491
Softening of water, 485
Solid metal solutions, 259
Solid solutions, 141, 265
Solid state, 106
Solubility, 134
Solubility product, 197
Solution, 132
  boiling and freezing points of, 144
  energy effect of, 137
  interstitial, 141
  ionisation and dissociation in, 144
  Mendeleev's chemical theory of, 134
  solid, 141, 259
  solid metal, 259
  substitutional, 141
Solvates, 134
Solvolysis, 215
Spatial configuration of molecules and complexes, 79
Spatial orientation of orbitals, 25
Spectroscopy, 147
Sphalerite, 467, 629
Spinel, 265, 457
Spin quantum number, 29
Spodumene, 420, 487
Stability constant of complex compounds, 193
Standard electrode potential, 226
Standard entropy, 179
Standard free energy of formation, 182
States of aggregation, 106
Strontianite, 481
Structural types of inorganic compounds, 110

Structure
  chain, 111
  coordination, 113
  insular, 111
  ionic compound, 95
  layered, 111, 113
Substance, 13
Sulphur, 326
Sulvanite, 540
Superoxide, 319
Superphosphate, 381
Sylvinite, 292, 492
Sylvite, 492
Synthesis of elements, 660

Tantalite, 540
Tantalum, 540
Tautomerism, 334
Technetium, 567
Tectohydrates, 268
Tellurium, 341
Temperature
  effect on direction of process, 181
    on equilibrium constant, 187
Ternary complexes, 263
Thallium, 464
Theory of localized electron pairs, 82
Thermodynamics, 167
Thorite, 647
Thortveitite, 420
Tinstone, 424
Titanium, 528
Tombac, 620
Tremolite, 420
Tridymite, 419
Tritium, 278
Tungsten, 548
Turnbull's blue, 589
Type metal, 426

Uncertainty principle, 19

Valence, 74
Valence angle, 50
Valence bond theory, 74
Vanadite, 540
Vanadium, 541
Van der Waals' forces, 98
Van't Hoff's isochore, 205
Velocity constant, 201
Velocity of chemical reaction, 198, 200
  instantaneous, 199
Vitallum, 594
Virial theory, 55
Visible and ultraviolet spectroscopy, 152
Vitriols, 338
Voltaic cell, 229

Wadeite, 420
Water gas, 280
Wave equation, 21
Wave function, 20
Witherite, 481
Wolframite, 549
Wood's metal, 385
Wurtzite, 467

X-Ray crystallography, 158
X-Ray spectroscopy, 148

Zeolites, 485
Zero overlapping, 61
Zinc, 628
Zinc blende, 629
Zircon, 420
Zirconium, 528

TO THE READER

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MENDELEEV'S PERIODI

Periods	I a	I b	II a	II b	III a	III b	IV a	IV b	V a
1	H								
2	3 Li 6.94$_1$ Lithium $2s^1$		4 Be 9.01218 Beryllium $2s^2$		5 B 10.81 Boron $2s^2\,2p^1$		6 C 12.011 Carbon $2s^2\,2p^2$		7 N 14.0067 Nitrogen
3	11 Na 22.98977 Sodium $3s^1$		12 Mg 24.305 Magnesium $3s^2$		13 Al 26.98154 Aluminium $3s^2\,3p^1$		14 Si 28.08$_6$ Silicon $3s^2\,3p^2$		15 P 30.97376 Phosphoru
4	19 K 39.09$_8$ Potassium $4s^1$		20 Ca 40.08 Calcium $4s^2$		21 Sc 44.9559 $3d^14s^2$ Scandium		22 Ti 47.90 $3d^24s^2$ Titanium		2 50 $3d^34s^2$ Van
	29 Cu 63.54$_6$ $3d^{10}4s^1$ Copper		30 Zn 65.38 $3d^{10}4s^2$ Zinc		31 Ga 69.72 $4s^24p^1$ Gallium		32 Ge 72.5$_9$ $4s^24p^2$ Germanium		33 As 74.9216 Arsenic
5	37 Rb 85.467$_8$ Rubidium $5s^1$		38 Sr 87.62 Strontium $5s^2$		39 Y 88.9059 $4d^15s^2$ Yttrium		40 Zr 91.22 $4d^25s^2$ Zirconium		41 92 $4d^45s^1$ Ni
	47 Ag 107.868 $4d^{10}\,5s^1$ Silver		48 Cd 112.40 $4d^{10}5s^2$ Cadmium		49 In 114.82 $5s^2\,5p^1$ Indium		50 Sn 118.6$_9$ $5s^2\,5p^2$ Tin		51 Sb 121.7$_5$ Antimony
6	55 Cs 132.9054 Cesium $6s^1$		56 Ba 137.3$_4$ Barium $6s^2$		57 La * 138.905$_5$ $5d^16s^2$ Lanthanum		72 Hf 178.4$_9$ $5d^26s^2$ Hafnium		73 180 $5d^36s^2$ Tant
	79 Au 196.9665 $5d^{10}6s^1$ Gold		80 Hg 200.5$_9$ $5d^{10}6s^2$ Mercury		81 Tl 204.3$_7$ $6s^26p^1$ Thallium		82 Pb 207.2 $6s^26p^2$ Lead		83 Bi 208.9804 Bismuth
7	87 Fr [223] Francium $7s^1$		88 Ra [226] Radium $7s^2$		89 Ac ** [227] $6d^17s^2$ Actinium		104 (Ku) [261] $6d^27s^2$ Kurchatovium		105 (N (Nilsboh

* LANTHANIDES

58 Ce $6s^2$ 140.12 $5d^1$ Cerium $4f^1$	59 Pr 140.9077 $4f^36s^2$ Praseodymium	60 Nd 144.2$_4$ $4f^46s^2$ Neodymium	61 Pm [145] $4f^56s^2$ Promethium	62 Sm 150.4 $4f^66s^2$ Samarium	63 Eu 151.96 $4f^76s^2$ Europium	64 G 157.2$_5$ Gadoli

** ACTINIDES

90 Th 232.0381 Thorium $6d^27s^2$	91 Pa $7s^2$ [231] $6d^15f^2$ Protactinium	92 U $7s^2$ 238.02$_9$ $6d^15f^3$ Uranium	93 Np $7s^2$ [237] $6d^15f^4$ Neptunium	94 Pu [244] $5f^67s^2$ Plutonium	95 Am [243] $5f^77s^2$ Americium	96 C [247] Curium

TABLE OF THE ELEMENTS

b	VI a	VI b	VII a	VII b	VIII a	VIII b
			1 H 1.0079 $1s^1$ Hydrogen		2 He 4.00260 $1s^2$ Helium	
$2p^3$	8 O 15.9994 $2s^2 2p^4$ Oxygen		9 F 18.99840 $2s^2 2p^5$ Fluorine		10 Ne 20.179 $2s^2 2p^6$ Neon	
$3p^3$	16 S 32.06 $3s^2 3p^4$ Sulphur		17 Cl 35.453 $3s^2 3p^5$ Chlorine		18 Ar 39.948 $3s^2 3p^6$ Argon	
V 41.4 um	24 Cr $3d^5 4s^1$ 51.996 Chromium		25 Mn $3d^5 4s^2$ 54.9380 Manganese		26 Fe $3d^6 4s^2$ 55.847 Iron	27 Co $3d^7 4s^2$ 58.9332 Cobalt	28 Ni $3d^8 4s^2$ 58.70 Nickel
$4p^3$	34 Se 78.96 $4s^2 4p^4$ Selenium		35 Br 79.904 $4s^2 4p^5$ Bromine		36 Kr 83.80 $4s^2 4p^6$ Krypton		
b 64 um	42 Mo $4d^5 5s^1$ 95.94 Molybdenum		43 Tc $4d^5 5s^2$ [97] Technetium		44 Ru $4d^7 5s^1$ 101.07 Ruthenium	45 Rh $4d^8 5s^1$ 102.9055 Rhodium	46 Pd $4d^{10} 5s^0$ 106.4 Palladium
$5p^3$	52 Te 127.60 $5s^2 5p^4$ Tellurium		53 I 126.9045 $5s^2 5p^5$ Iodine		54 Xe 131.30 $5s^2 5p^6$ Xenon		
a 179 m	74 W $5d^4 6s^2$ 183.85 Tungsten		75 Re $5d^5 6s^2$ 186.207 Rhenium		76 Os $5d^6 6s^2$ 190.2 Osmium	77 Ir $5d^7 6s^2$ 192.2 Iridium	78 Pt $5d^9 6s^1$ 195.09 Platinum
$6p^4$	84 Po [209] $6s^2 6p^4$ Polonium		85 At [210] $6s^2 6p^5$ Astatine		86 Rn [222] $6s^2 6p^6$ Radón		
s) 61] m)	106 E-W [263]		107 E-Re [261]				

$4f^9$	65 Tb 158.9254 $4f^9 6s^2$ Terbium	66 Dy 162.50 $4f^{10} 6s^2$ Dysprosium	67 Ho 164.9304 $4f^{11} 6s^2$ Holmium	68 Er 167.26 $4f^{12} 6s^2$ Erbium	69 Tm 168.9342 $4f^{13} 6s^2$ Thulium	70 Yb 173.04 $4f^{14} 6s^2$ Ytterbium	71 Lu 174.97 $4f^{14} 5d^1 6s^2$ Lutetium
1	97 Bk [247] $5f^9 7s^2$ Berkelium	98 Cf [251] $5f^{10} 7s^2$ Californium	99 Es [254] $5f^{11} 7s^2$ Einsteinium	100 Fm [257] $5f^{12} 7s^2$ Fermium	101 Md [258] $5f^{13} 7s^2$ Mendelevium	102 (No) [259] $5f^{14} 7s^2$ (Nobelium)	103 (Lr) [260] $5f^{14} 6d^1 7s^2$ Lawr